Hydrogen-bonding interactions and magnetic relaxation dynamics in tetracoordinated cobalt(II) single-ion magnets

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Fig. S14 Cole–Cole plot for **1**·CH₃OH under 1400 Oe dc field from 1.9 to 8 K. The solid lines represent the fit to a generalized Debye model.

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Fig. S17 Temperature dependence of the relaxation time τ under dc field for 1·CH-₃OH. The dashed lines indicate fitted lines for a single relaxation process of phonon-bottleneck-limited direct process (grey) and Raman (green). The solid black line indicates the sum of relaxation processes. $C = 1.40 \times 10^{-3} \text{ s}^{-1} \text{ K}^{-8.0}$, n = 8.0, and $B = 1.84 \text{ s}^{-1} \text{ K}^{-2}$).

Fig. S18 Field dependence of the relaxation time τ for **3** at 4 K. The dashed lines indicate fitted lines for a single relaxation process of direct process $\tau^{-1} = ATH^2$ (blue), Raman $\tau^{-1} = CT^n$ (green), and QTM $\tau^{-1} = B_1/(1+B_2H^2)$ (magenta). The solid black line indicates the sum of relaxation processes. A = 0.157 K⁻¹ kOe⁻² s⁻¹, $C = 6.18 \times 10^{-4}$ s⁻¹ K^{-6.3}, n = 6.3, $B_1 = 248.9$ s⁻¹ and $B_2 = 492.1$ kOe⁻².

5. Powder X-ray diffraction measurement.

Fig. S19 Room-temperature powder XRD patter of $1 \cdot CH_3OH$ 11 months after isolation, and the corresponding simulated pattern from single-crystal X-ray analysis at 90 K. These patterns suggest that the methanol molecule of crystallization in $1 \cdot CH_3OH$ is tightly bounded by hydrogen-bond and the $1 \cdot CH_3OH$ does not easily lose methanol molecule upon standing.

1. Experimental

All chemicals were used as purchased without further purification unless noted. The ligand precursors H_2 iml, H_2 imn and H_2 thp were prepared according to previously reported methods.¹

Synthesis of $[Co(Himl)_2]$ ·MeOH: A methanol solution (5 mL) of CoCl₂·6H₂O (47.5 mg, 0.20 mmol) was slowly added to a methanol solution (5 mL) of H₂iml (64.2 mg, 0.40 mmol) and NMe₄OH·5H₂O (72.3 mg, 0.40 mmol) in a Schlenk flask under Ar atmosphere. The reaction mixture was allowed to stand at room temperature under Ar for a few days, and red crystals were obtained. Yield: 65.3 mg, 80%. Anal. Calcd for $[Co(Himl)_2]$ ·CH₃OH = C₁₉H₁₈CoN₄O₃: C, 55.75; H, 4.43; N, 13.69%. Found: C, 55.70; H, 4.25; N, 13.60%.

Synthesis of $[Co(Himn)_2]$: A methanol solution (5 mL) of $CoCl_2 \cdot 6H_2O$ (48.3 mg, 0.20 mmol) was slowly added to a methanol solution (5 mL) of H₂imn (65.9 mg, 0.41 mmol) and KO'Bu (47.5 mg, 0.42 mmol) in a Schlenk flask under Ar atmosphere. The reaction mixture was allowed to stand at room temperature under Ar for a few days, and red crystals were obtained. Yield: 54.5 mg, 71%. Anal. Calcd for $[Co(Himn)_2] = C_{18}H_{18}CoN_4O_2$: C, 56.70; H, 4.76; N, 14.69%. Found: C, 56.40; H, 4.38; N, 14.40%.

Synthesis of $[Co(Hthp)_2]$: A ethanol solution (5 mL) of CoBF₄·6H₂O (68.8 mg, 0.20 mmol) was slowly added to an ethanol solution (5 mL) of H₂thp (72.5 mg, 0.41 mmol) and KO'Bu (45.4 mg, 0.40 mmol) in a Schlenk flask under Ar atmosphere. The reaction mixture was allowed to stand at room temperature under Ar for a few days, and red crystals were obtained. Yield: 34.5 mg, 42%. Anal. Calcd for $[Co(Hthp)_2]$ =C₂₀H₂₂CoN₄O₂: C, 58.68; H, 5.42; N, 13.69%. Found: C, 58.32; H, 5.09; N, 13.57%.

2. X-ray crystallography

X-ray diffraction data were obtained at 90(2) K with a Bruker SMART APEX equipped with CCD detector with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). A

¹ R. Mitsuhashi, T. Suzuki, Y. Sunatsuki, Inorg. Chem. 2013, 52, 10183–10190.

single crystal was mounted with a glass capillary and flash cooled with a cold nitrogen gas stream. Data were processed using SMART software packages. Absorption corrections were applied using empirical methods.² Structures were solved using the intrinsic phasing method employing the SHELXT software package³ and refined on F^2 (with all independent reflections) using the SHELXL software package.⁴ In the X-ray analysis, all hydrogen atoms were located by using a riding model, except for the H atom at the N–H bonds, which was located from the electron-density difference maps and refined isotropically.

The crystal structure of $1 \cdot CH_3OH$ was isomorphous to the Zn^{II} analogue whereas that of **2**, [Zn(Himn)₂]·CH₃OH, contained a methanol molecule as solvent of crystallization.⁵

² Bruker, *SADABS*, Program for Absorption Correction; Bruker AXS Inc., Madison, Wisconsin, USA, 2001.

³ G. M. Sheldrick, Acta Crystallogr. Sect. A Found. Adv. 2015, 71, 3.

⁴ G. M. Sheldrick, Acta Crystallogr. Sect. C Struct. Chem. 2015, 71, 3.

⁵ (a) H.-S. He, *Acta Crystallogr. Sect. E: Struct. Rep. Online* 2006, **62**, m3042–m3043. (b) H.-S. He, *Acta Crystallogr. Sect. E: Struct. Rep. Online* 2007, **63**, m344–m345.

Complex	[Co(Himl)2]·CH3OH	[Co(Himn) ₂]	[Co(Hthp) ₂]
Chemical formula	$C_{19}H_{18}CoN_4O_3$	$C_{18}H_{18}CoN_4O_2$	$C_{20}H_{22}CoN_4O_2$
Formula weight	409.30	381.29	409.34
Color and shape of crystal	red, needle	red, prism	purple, platelet
Size of specimen (mm ³)	$0.36 \times 0.12 \times 0.12$	$0.45 \times 0.20 \times 0.20$	$0.30 \times 0.30 \times 0.20$
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	Pbca	$P2_{1}/n$	C2/c
<i>a</i> / Å	9.6795(11)	11.9830(19)	13.789(3)
<i>b</i> / Å	14.4187(16)	7.6704(13)	11.399(3)
<i>c</i> / Å	25.494(3)	18.692(3)	12.212(3)
α / °	90	90	90
eta / °	90	105.227(2)	116.361(4)
γ/°	90	90	90
$V/ Å^3$	3558.1(7)	1657.8(5)	1720.0(7)
Ζ	8	4	4
T / K	90(2)	90(2)	90(2)
$D_{ m calc}$ / g cm ⁻³	1.528	1.528	1.581
F (000)	1688	788	852
μ (Mo-K _a) / mm ⁻¹	0.993	1.055	1.023
$R_{ m int}$	0.0382	0.0378	0.0367
$2 heta_{ m max}$ / °	57	57	57
No. of independent reflection	4417	3976	2101
$R_1(F^2: F_o^2 > 2s (F_o^2))$	0.0363	0.0419	0.0403
wR_2 (F^2 : all data)	0.0946	0.1006	0.1231

 Table S1. Crystallographic information.

 $\overline{R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|, wR_2} = [\Sigma (F_o^2 - F_c^2) / \Sigma w (F_o^2)^2]^{1/2}$

Table S2. Selected bond distances, angles, and dihedral angles (Å, °).

	[Co(Himl) ₂]·CH ₃ OH	[Co(Himn) ₂]	[Co(Hthp) ₂]
Co1–O1	1.9220(13)	1.9389(16)	1.9184(17)
Co1–O2	1.9309(13)	1.9357(16)	
Co1–N2	1.9776(15)	1.9593(18)	1.9551(19)
Co1–N4	1.9566(16)	1.9586(18)	
N1-C7	1.349(2)	1.362(3)	1.354(3)
N2-C7	1.341(2)	1.308(3)	1.315(3)
N3-C16	1.354(2)	1.361(3)	
N4C16	1.338(2)	1.311(3)	
O1–Co1–O2(O1 ⁱ)	118.68(6)	109.91(7)	108.84(10)
N2-Co1-N4(N2 ⁱ)	126.70(6)	126.30(8)	125.99(11)
O1–Co1–N2	93.11(6)	93.56(7)	96.93(7)
O1–Co1–N4(N2 ⁱ)	116.15(6)	120.02(7)	114.06(8)
O2-Co1-N2	109.50(6)	113.33(7)	
O2-Co1-N4	94.67(6)	94.25(7)	
$ au_4$	0.81	0.81	0.85

Symmetry code: (i = -x+1, y, -z+3/2)

Table S3. Flattening and rocking distortions of the coordination geometries between two chelating ligands. Selected dihedral angles of mean planes (°).

	[Co(Himl) ₂]·CH ₃ OH	[Co(Himn) ₂]	[Co(Hthp) ₂]
Flattening distortion			
plane(O1,Co1,N2)-plane(O2,Co1,N	N4) 81.93(9)	89.80(10)	88.63(11)
Rocking distortion			
plane(O1,Co1,N2)-Co1-O2(O1 ⁱ)	53.12(7)	57.38(9)	56.37(10)
plane(O2,Co1,N4)-Co1-O1	47.18(7)	51.13(8)	
Average	50.2(1)	54.3(1)	
plane(O1,Co1,N2)-Co1-N4(N2 ⁱ)	40.30(8)	36.88(9)	40.52(10)
plane(O2,Co1,N4)-Co1-N2	44.74(8)	42.43(9)	
Average	45.5(1)	39.7(1)	

Symmetry code: (i = -x+1, y, -z+3/2)

Table S4 Hydrogen-bond distances (Å) and angles (°).

	D	Н	А	D–H	Н…А	D····A	D–H…A
[Co(Himn) ₂]	N1	H1	$O2^i$	0.84(3)	2.03(3)	2.845(3)	164(3)
	N3	H3A	O1 ⁱⁱ	0.83(3)	2.03(3)	2.844(2)	165(2)
[Co(Himl) ₂]·CH ₃ OH	N1	H1	O2 ⁱⁱⁱ	0.86(3)	1.95(3)	2.766(2)	156(2)
	O3	H3M	01	0.84	1.81	2.6483(19)	171.7
	N3	H3A	O3 ⁱⁱ	0.83(3)	1.94(3)	2.752(2)	164(2)
[Co(Hthp) ₂]	N1	H1N	$O1^{iv}$	0.81(3)	2.29(3)	3.059(3)	158(3)

Symmetry code: (i = '-x, -y+1, -z+1', ii = '-x+1, -y+1, -z+1', iii = 'x-1/2, y, -z+3/2 ', iv = 'x, -y+1, z-1/2 ').

Table S5 Intra- and interchain Co…Co distances (Å).

	Intrachain			Interchain		
[Co(Himn) ₂]	Co1	Co1 ⁱ	6.254(1)	Co1	Co1 ⁱⁱⁱ	7.6704(13)
	Co1	Co1 ⁱⁱ	6.048(1)			
[Co(Himl) ₂]·CH ₃ OH	Co1	Co1 ^{iv}	7.029(1)	Co1	Co1	7.937(1)
[Co(Hthp) ₂]	Co1	Co1 ^v	6.359(1)	Co1	Co1 ^{vi}	8.945(3)

Symmetry code: (i = '-x, -y+1, -z+1', ii = '-x+1, -y+1, -z+1', iii = 'x, y+1, z', iv = '-x, -y, -z', v = 'x, -y+1, z-1/2', vi = 'x+1/2, y+1/2, z').



Fig. S1 Molecular structures of (a) 1 in $1 \cdot CH_3OH$, (b) 2 and (c) 3 (50% probability levels).



Fig. S2 Hydrogen-bonded sheet structure in $1 \cdot CH_3OH$. Views (a) from the *b* axis and (b) from the *a* axis. Intra-sheet Co^{II...}Co^{II} distances (7.03 and 7.94 Å) and inter-sheet distance (7.51 Å) are shown.



Fig. S3 Hydrogen-bonded chain structure in **2** (view from the *a* axis). The interchain $Co^{II} \cdots Co^{II}$ distances (9.43 and 10.79 Å) are shown.



Fig. S4 Hydrogen-bonded chain structure in **3** (view from the *c* axis). The interchain $Co^{II}...Co^{II}$ distance (8.95 Å) is shown.

3. Diffuse reflectance spectra



Fig. S5 Diffuse reflectance spectra of 1·CH₃OH (green), 2 (red) and 3 (blue).

4. Magnetic measurements.

Magnetic susceptibility measurements were performed with a MPMS-XL7 or MPMS-7 SQUID magnetometer. Susceptibility data were obtained in the temperature range from 1.9 to 300 K with static field of 0.5 T. The polycrystalline samples were ground into fine powders by an agate mortar. The samples were loaded into a gelatin capsule and covered in liquid paraffin to prevent field-induced orientation of crystals. All data were corrected for diamagnetism of the sample by means of Pascal's constants. The dynamic susceptibility was measured with alternating-current (ac) fields of 3 Oe magnitude and a constant direct current (dc) field of 0–5000 Oe in the frequency range from 0.03 to 1500 Hz.

Static magnetic properties



Fig. S6 (a) Temperature dependence of $\chi_M T$ product for **1**·CH₃OH in applied field 5000 Oe. (b) Field dependence of magnetization for **1**·CH₃OH at 2, 4, 6, and 8 K. Solid points are the experimental data and the solid lines correspond to the fit.



Fig. S7 (a) Temperature dependence of $\chi_M T$ product for **3** in applied field 5000 Oe. (b) Field dependence of magnetization for **3** at 2, 4, 6, and 8 K. Solid points are the experimental data and the solid lines correspond to the fit.



Fig. S8 Temperature dependence of (a) the in-phase χ'_M vs. frequency plots and (b) out-of-phase χ''_M vs. frequency plots for **1**·CH₃OH in 1400 Oe dc field with ac frequency of 0.1–1488 Hz. The lines are a guide for the eye.



Fig. S9 Temperature dependence of (a) the in-phase χ'_M vs. frequency plots and (b) out-of-phase χ''_M vs. frequency plots for **2** in zero Oe dc field with ac frequency of 0.1–1488 Hz (1.9 K–8.0 K). The lines are a guide for the eye.



Fig. S10 Temperature dependence of (a) the in-phase χ'_M vs. frequency plots and (b) out-of-phase χ''_M vs. frequency plots for **2** in 400 Oe dc field with ac frequency of



0.1–1488 Hz (1.9 K–8.0 K). The lines are a guide for the eye.

Fig. S11 Temperature dependence of (a) the in-phase χ'_M vs. frequency plots and (b) out-of-phase χ''_M vs. frequency plots for **3** in zero Oe dc field with ac frequency of 1–1488 Hz (1.9 K–8.0 K). The lines are a guide for the eye.



Fig. S12 Temperature dependence of (a) the in-phase χ'_M vs. frequency plots and (b) out-of-phase χ''_M vs. frequency plots for **3** in 800 Oe dc field with ac frequency of 0.03–1488 Hz (2.8 K–8.0 K). The lines are a guide for the eye.



Fig. S13 Dc field dependence of (a) the in-phase χ'_M vs. frequency plots and (b) out-of-phase χ''_M vs. frequency plots for **3** with ac frequency of 0.1–148.8 Hz at 4 K. The lines are a guide for the eye.

Debye model fit

The ac susceptibility data for 1, 2·CH₃OH and 3 were fitted by using a generalized Debye model CC-fit program, and the relaxation time τ and dispersion coefficient α .



Fig. S14 Cole–Cole plot for **1**·CH₃OH under 1400 Oe dc field from 1.9 to 8 K. The solid lines represent the fit to a generalized Debye model.



Fig. S15 Cole–Cole plot for **2** (a) under zero dc field and (b) under 400 Oe dc field from 1.9 to 8 K. The solid lines represent the fit to a generalized Debye model.



Fig. S16 Cole–Cole plot for **3** (a) under zero dc field and (b) under 800 Oe dc field from 1.9 to 7 K. The solid lines represent the fit to a generalized Debye model.



Fig. S17 Temperature dependence of the relaxation time τ under dc field for 1·CH₃OH. The dashed lines indicate fitted lines for a single relaxation process of phonon-bottleneck-limited direct process (grey) and Raman (green). The solid black line indicates the sum of relaxation processes. $C = 1.40 \times 10^{-3} \text{ s}^{-1} \text{ K}^{-8.0}$, n = 8.0, and $B = 1.84 \text{ s}^{-1} \text{ K}^{-2}$).



Fig. S18 Field dependence of the relaxation time τ for 3 at 4 K. The dashed lines indicate fitted lines for a single relaxation process of direct process $\tau^{-1} = ATH^2$ (blue), Raman $\tau^{-1} = CT^n$ (green), and QTM $\tau^{-1} = B_1/(1+B_2H^2)$ (magenta). The solid black line indicates the sum of relaxation processes. A = 0.157 K⁻¹kOe⁻²s⁻¹, $C = 6.18 \times 10^{-4}$ s⁻¹ K^{-6.3}, n = 6.3, $B_1 = 248.9$ s⁻¹ and $B_2 = 492.1$ kOe⁻².

5. Powder X-ray diffraction measurement.

Powder XRD data was collected at room temperature on a Rigaku RINT 2100 powder diffractometer using Cu K α radiation ($\lambda = 1.5418$ Å). The sample was ground in an agate mortar and placed on a silicon sample holder. The simulated powder pattern was calculated from the cif using the Mercury 3.8 software.



Fig. S19 Room-temperature powder XRD patter of $1 \cdot CH_3OH$ 11 months after isolation, and the corresponding simulated pattern from single-crystal X-ray analysis at 90 K. These patterns suggest that the methanol molecule of crystallization in $1 \cdot CH_3OH$ is tightly bounded by hydrogen-bond and the $1 \cdot CH_3OH$ does not easily lose methanol molecule upon standing.