Supporting Information

Field-induced single-molecule magnet behavior in ideal trigonal antiprismatic cobalt(II) complexes: precise geometrical control by a hydrogen-bonded rigid metalloligand

Ryoji Mitsuhashi,^a* Kasper S. Pedersen,^b Takaaki Ueda,^a Takayoshi Suzuki^{c,d}, Jesper Bendix^e, and Masahiro Mikuriya^a

- ^a Department of Applied Chemistry for Environment, School of Science and Technology, Kwansei Gakuin University, 2-1 Gakuen, Sanda, Hyogo 669-1337, Japan
- ^b Department of Chemistry, Technical University of Denmark, 2800 Kongens Lyngby, Denmark
- ^c Department of Chemistry, Faculty of Science, Okayama University, 3-1-1 Tsushima-naka, Kita-ku, Okayama 700-8530, Japan
- ^d Research Institute for Interdisciplinary Science, Okayama University, 3-1-1 Tsushima-naka, Kita-ku, Okayama 700-8530, Japan
- ^e Department of Chemistry, University of Copenhagen, Universitets Parken, 5, 2100, Copenhagen Denmark

E-mail: mitsuhashi@kwansei.ac.jp

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 $[Co_3(Himn)_6](NO_3)_2 \cdot 2CH_3OH.$

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3. Powder XRD

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4. Magnetic Measurements

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1. Experimental

All chemicals were used as purchased without further purification, unless noted. The ligand precursor H_2 imn was prepared according to a previously reported method.¹ Elemental analyses were performed at the Department of Instrumental Analysis, Advanced Science Research Center, Okayama University.

 $[Co_3(Himn)_6]Cl_2 \cdot 2CH_3OH$: To a methanol solution (10 mL) of CoCl₂ · 6H₂O (47.3 mg, 0.20 mmol) and H₂imn (97.5 mg, 0.60 mmol) was slowly added a methanol solution of KO'Bu (68.3 mg, 0.61 mmol). The reaction mixture was stirred overnight at room temperature in air and then evaporated to dryness. A green residue was obtained. This residue was dissolved in methanol (5 mL). The solution was degassed by bubbling N₂ gas, and then a 10 mL methanol solution of CoCl₂·6H₂O (23.7 mg, 0.10 mmol) was added. The reaction mixture was allowed to stand at room temperature under N₂ for a month, and reddish-brown crystals were obtained. Yield: 43.6 mg, 34%. Anal. Calcd for $[Co_3(Himn)_6]Cl_2 \cdot 2CH_3OH = C_{56}H_{62}Cl_2Co_3N_{12}O_8$: C, 52.59; H, 4.89; N, 13.14%. Found: C, 52.54; H, 4.65; N, 13.24%.

 $[Co_3(Himn)_6]Br_2 \cdot 2CH_3OH$: To a methanol solution (10 mL) of $CoBr_2 \cdot 6H_2O$ (65.6 mg, 0.20 mmol) and H_2 imn (97.7 mg, 0.60 mmol) was slowly added a methanol solution of KO'Bu (67.5 mg, 0.60 mmol). The reaction mixture was stirred overnight at room temperature in air and then evaporated to dryness. A green residue was obtained. This residue was dissolved in methanol (5 mL) and insoluble white residue was removed by

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

filtration. The filtrate was degassed by bubbling N₂ gas, and then a methanol solution of $CoBr_2 \cdot 6H_2O$ (32.0 mg, 0.10 mmol) was added. The reaction mixture was allowed to stand at room temperature under N₂ for two weeks, and reddish-brown crystals were obtained. Yield: 52.8 mg, 37%. Anal. Calcd for $[Co_3(Himn)_6]Br_2 \cdot 3CH_3OH \cdot H_2O = C_{57}H_{72}Br_2Co_3N_{12}O_{12}$: C, 47.09; H, 4.99; N, 11.56%. Found: C, 46.97; H, 4.75; N, 11.61%

[Co₃(Himn)₆]I₂·2CH₃OH: To a methanol solution (10 mL) of CoI₂·*n*H₂O (82.7 mg) and H₂imn (98.6 mg, 0.61 mmol) was slowly added a methanol solution of KO'Bu (67.5 mg, 0.60 mmol). The reaction mixture was stirred overnight at room temperature in air and then evaporated to dryness. A green residue was obtained. This residue was dissolved in methanol (5 mL) and insoluble white residue was removed by filtration. The filtrate was degassed by bubbling N₂ gas, and then a 10 mL methanol solution of CoI₂·*n*H₂O (41.2 mg, mmol) was added. The reaction mixture was allowed to stand at room temperature under N₂ for two weeks, and reddish-brown crystals were obtained. Yield: 80.2 mg. Anal. Calcd for [Co₃(Himn)₆]I₂·2CH₃OH·3H₂O = C₅₆H₆₈Co₃I₂N₁₂O₁₁: C, 44.37; H, 4.52; N, 11.09%. Found: C, 44.09; H, 4.09; N, 11.32%.

[Co₃(Himn)₆](NO₃)₂·2CH₃OH: To a methanol solution (10 mL) of Co(NO)₂·6H₂O (57.8 mg, 0.20 mmol) and H₂imn (97.4 mg, 0.60 mmol) was slowly added NEt₃ (80 μ L). After being stirred for a night in air, a green solution of *mer*-[Co(Himn)₃] was obtained. The green solution was degassed by bubbling N₂ gas, and then a methanol solution of Co(NO₃)₂·6H₂O (30.0 mg, 0.10 mmol) was added. The reaction mixture was allowed to stand at room temperature under N₂ for one week, and reddish-brown crystals were obtained. Yield: 81.3 mg, 57%. Anal. Calcd for [Co₃(Himn)₆](NO₃)₂·2CH₃OH·2.3H₂O = C₅₆H_{66.6}Co₃N₁₄O_{16.3}: C, 48.97; H, 4.89; N, 14.28%. Found: C, 48.50; H, 4.32; N, 14.65%.

2. X-Ray crystallography

Single-crystal X-ray diffraction data were collected at -183(2) °C, using a Bruker SMART APEX diffractometer system with graphite-monochromated Mo K α radiation $(\lambda = 0.71073 \text{ Å})$. A single crystal was mounted on a glass fiber and flash-cooled with a cold N₂ gas stream. Data were processed using the Bruker APEX III software packages. Absorption corrections were applied using empirical methods.² Structures were solved using the intrinsic phasing methods, as implemented in the SHELXT.³ All structures were refined on F^2 (with all independent reflections) using the SHELXL.⁴ In X-ray analysis, all H atoms at N-H bonds were located using electron density difference maps, and were refined isotropically. Reflections caused by solvent disorder located in void spaces were treated using the SQUEEZE program.⁵ In [Co₃(Himn)₆]Br₂·2CH₃OH and [Co₃(Himn)₆](NO₃)₂·2CH₃OH, ~18 electrons were removed from 18 solvent-accessible voids (50–55 Å³/void) from the unit cell (355 and 302 electrons in total, respectively). These correspond to three methanol molecules per formula. The elemental analysis indicated that these three methanol molecules tend to be lost or be substituted by H₂O molecules. As the formula weight of the disordered solvents of crystallization must be small compared to the entire formula, all the complex salts are regarded as $[Co_3(Himn)_6]X_2 \cdot 2CH_3OH$ for simplicity.

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, 3–8.

⁴ G. M. Sheldrick, Acta Crystallogr., Sect. C: Struct. Chem. 2015, 71, 3–8.

⁵ A. L.Spek, Acta Crystallogr., Sect. C: Struct. Chem. 2015, 71, 9–18.

Complex	1Cl ₂ ·2CH ₃ OH	1Br ₂ ·2CH ₃ OH	$1(NO_3)_2 \cdot 2CH_3OH$
Chemical formula	$C_{56}H_{62}Cl_2Co_3N_{12}O_8$	$C_{56}H_{62}Br_2Co_3N_{12}O_8$	$C_{56}H_{62}Co_{3}N_{14}O_{14}$
Formula weight	1278.86	1367.78	1331.98
Color and shape of crystal	brown, block	brown, platelet	brown, platelet
Size of specimen (mm ³)	$0.20\times0.08\times0.04$	$0.24 \times 0.22 \times 0.03$	$0.38 \times 0.32 \times 0.26$
Crystal system	trigonal	trigonal	trigonal
Space group	RĪ	$R\bar{3}c$	$R\bar{3}c$
<i>a</i> / Å	11.349(2)	11.0654(11)	11.169(3)
<i>b</i> / Å	11.349(2)	11.0654(11)	11.169(3)
<i>c</i> / Å	38.211(7)	87.132(9)	87.48(2)
lpha / °	90	90	90
β/°	90	90	90
γ / °	120	120	120
V / Å ³	4262.4(17)	9239(2)	9450(5)
Ζ	3	6	6
T / K	90(2)	90(2)	90(2)
$D_{ m calc}$ / g cm $^{-3}$	1.495	1.475	1.404
F (000)	1983	4182	4134
μ (Mo-K _a) / mm ⁻¹	1.025	2.157	0.853
$R_{\rm int}$	0.0538	0.0733	0.0639
$2 heta_{ m max}$ / °	57	57	57
No. of independent reflections	2353	2589	2631
$R_1(F^2: F_o^2 > 2s (F_o^2))$	0.0603	0.0766	0.0423
wR_2 (F^2 : all data)	0.1645	0.1458	0.1091

Table S1. Crystallographic information.

 $R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|, wR_{2} = [\Sigma (F_{o}^{2} - F_{c}^{2}) / \Sigma w (F_{o}^{2})^{2}]^{1/2}$

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

		\mathcal{O}	
	$1Cl_2 \cdot 2CH_3OH$	1Br ₂ ·2CH ₃ OH	$1(NO_3)_2 \cdot 2CH_3OH$
Co1-O1	1.906(2)	1.910(3)	1.909(2)
Co1–N2	1.896(3)	1.895(4)	1.890(2)
Co2–O1	2.076(2)	2.083(3)	2.066(2)
Co1…Co2	2.743(1)	2.751(2)	2.727(1)
$O1-O1^a$	2.496(3)	2.502(6)	2.501(3)
O1-Co1-N2	93.2(1)	93.0(2)	93.4(1)

O1–Co2–O1 ^a	73.9(1)	73.8(2)	74.5(1)
O1–Co1–N2 ^a	170.9(1)	171.8(2)	171.6(1)
O1–Co1–N2 ^b	90.0(1)	91.2(2)	90.7(1)
Co2–O1, O1, ^{<i>a</i>} O1 ^{<i>b</i>}	1.494(2)	1.501(3)	1.477(2)
s/h	0.84	0.83	0.85

Symmetry code (a = 1-y, x-y, z; b = 1-x+y, 1-x, z; c = 4/3-x, 2/3-y, 2/3-z)

Table S3. Hydrogen-bond distances and angles.

	D	Н	А	D–H / Å	H…A / Å	D…A /Å	D–H…A / °
$1Cl_2 \cdot 2CH_3OH$	N1	H1	Cl1	0.71(4)	2.44(4)	3.122(3)	160(4)
1Br ₂ ·2CH ₃ OH	N1	H1	Br1	0.75(5)	2.68(5)	3.347(5)	150(3)
1(NO ₃) ₂ ·2CH ₃ OH	N1	H1	02	0.87(3)	2.04(3)	2.880(2)	161(2)



Fig. S1 Hydrogen-bonding interactions in (a) $[Co_3(Himn)_6]Br_2 \cdot 2CH_3OH$, and (b) $[Co_3(Himn)_6](NO_3)_2 \cdot 2CH_3OH$ (non-hydrogen-bonded O atoms in the NO_3^- ion were omitted for clarity).



Fig. Packing diagrams compound **S2** the from (a) of the b axis [Co₃(Himn)₆]Cl₂·2CH₃OH, [Co₃(Himn)₆]Br₂·2CH₃OH, (b) and (c) $[Co_3(Himn)_6](NO_3)_2 \cdot 2CH_3OH.$



Fig. S3 NH···X···HN hydrogen bond angles in (a) $[Co_3(Himn)_6]Cl_2 \cdot 2CH_3OH$, (b) $[Co_3(Himn)_6]Br_2 \cdot 2CH_3OH$, and (c) $[Co_3(Himn)_6](NO_3)_2 \cdot 2CH_3OH$.

3. Powder XRD

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



Fig. S4 Room-temperature powder XRD patterns $[Co_3(Himn)_6]Cl_2 \cdot 2CH_3OH$, $[Co_3(Himn)_6]Br_2 \cdot 2CH_3OH$ and $[Co_3(Himn)_6]I_2 \cdot 2CH_3OH$, and the simulated patterns of $[Co_3(Himn)_6]Cl_2 \cdot 2CH_3OH$ and $[Co_3(Himn)_6]Br_2 \cdot 2CH_3OH$ from single-crystal X-ray analysis at 90 K. The diffraction pattern of the I⁻ salt is identical to that of the Br⁻ salt rather than the Cl⁻ salt suggesting the resemblance in their crystal structures.

4. Magnetic measurements

Magnetic measurements were carried out on a Quantum Design MPMS-XL7 SQUID or MPMS-7 magnetometer. The dc susceptibility measurements were conducted in an applied field of 3000–5000 Oe. For all measurements, the crystalline samples were ground into fine powders using an agate mortar. Over 20 mg of powder was loaded into a gelatin capsule, and covered in liquid paraffin to avoid field-induced orientation of the crystallites. All data were corrected for diamagnetism of the sample by means of Pascal's constants.



Fig. S5 Temperature dependence of the $\chi'_M T$ product in an applied field of 3000–5000 Oe. The solid lines correspond to the fit.



Fig. S6 The *M* vs *H* plots of (a) $1Cl_2 \cdot 2CH_3OH$, (b) $1Br_2 \cdot 2CH_3OH$, (c) $1I_2 \cdot 2CH_3OH$, and (d) $1(NO_3)_2 \cdot 2CH_3OH$ at 2, 4, 6 and 8 K. The dots and the solid lines indicate the experimental and simulated data using *g* and *D* values obtained from the best fits of χT vs *T* plots, respectively.



Fig. S7 Temperature dependence of (a) the in-phase χ'_M vs Frequency plots and (b) out-of-phase χ''_M vs Frequency plots for $1Cl_2 \cdot 2CH_3OH$ in 1400 Oe dc field with ac frequency of 1–1488 Hz. The lines are a guide for the eye.



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 $1Br_2 \cdot 2CH_3OH$ in 1200 Oe dc field with ac frequency of 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 $1I_2 \cdot 2CH_3OH$ in 2000 Oe dc field with ac frequency of 1–1488 Hz. The lines are a guide for the eyes.



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 $1(NO_3)_2 \cdot 2CH_3OH$ in 1200 Oe dc field with ac frequency of 1–1488 Hz. The lines are a guide for the eyes.



Fig. S11 Field (dc) dependence of (a) the in-phase χ'_{M} vs Frequency plots and (b) out-of-phase χ''_{M} vs Frequency plots for $1\text{Cl}_2 \cdot 2\text{CH}_3\text{OH}$ at 1.9 K with ac frequency of 1–1488 Hz. The lines are a guide for the eyes.



Fig. S12 Field (dc) dependence of (a) the in-phase χ'_M vs Frequency plots and (b) out-of-phase χ''_M vs Frequency plots for $1Br_2 \cdot 2CH_3OH$ at 1.9 K with ac frequency of 1–1488 Hz. The lines are a guide for the eyes.



Fig. S13 Field (dc) dependence of (a) the in-phase χ'_{M} vs Frequency plots and (b) out-of-phase χ''_{M} vs Frequency plots for $1I_2$ ·2CH₃OH at 1.9 K with ac frequency of 1–1488 Hz. The lines are a guide for the eyes.



Fig. S14 Field (dc) dependence of (a) the in-phase χ'_{M} vs Frequency plots and (b) out-of-phase χ''_{M} vs Frequency plots for $1(NO_3)_2 \cdot 2CH_3OH$ at 1.9 K with ac frequency of 1–1488 Hz. The lines are a guide for the eyes.