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Supporting Information

Impact of halogen ions on the guest dependent spin crossover behavior and porosity of Co(II) one-dimensional coordination polymers [Co (4'-(4-pyridyl)-2,2':6',2''-terpyridine)X_2] (X = Cl and Br)

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Experimental Sections

Synthesis

[$CoCl_2$(pyterpy)]·2H_2O (1·2H_2O)

Single crystals of **1·2H_2O** were prepared as follows. The pyterpy (1 equiv.) was dissolved in hot MeOH, then $CoCl_2$ (1 equiv.) in MeOH was added to the solution. This mixture was stirred at room temperature for 8h and a brown precipitate was obtained by filtration. Orange brown crystals of **1·2H_2O** were obtained by slow evaporation of the filtrate.

[$CoBr_2$(pyterpy)]·MeOH (2·MeOH)

Single crystals of **2·MeOH** were prepared by a literature method.[1] The pyterpy (1 equiv.) in MeOH was placed in one sidearm of an H-tube. $CoBr_2·6H_2O$ (1 equiv.) was placed in the other side, and MeOH was gently layered over both sides until the H-tube was full. After two weeks brown crystals of **2·MeOH** had formed. The MeOH solvent molecules were exchanged by H_2O from the atmosphere immediately after filatration to yield **2·H_2O**. **2·H_2O**: Anal. Calcd for $Br_2C_{20}CoH_{16}N_4O$: C, 43.91; H, 2.95; N, 10.24. Found: C, 43.61; H, 3.18; N, 10.21.

[1] S. Hayami, K. Hashiguchi, G. Juhasz, M. Ohba, H. Okawa, Y. Maeda, K. Kato, K. Osaka, M. Takata, K. Inoue, *Inorg. Chem.*, 2004, **43**, 4124.

Physical measurements

Temperature-dependent magnetic susceptibilities were measured by a Superconducting Quantum Interference Device (SQUID) magnetometer at field strengths of 1 T. X-ray powder diffraction (XRPD) patterns were performed on a Rigaku SmartLab X-ray difractometer (RAD-2A with a 2.0 kW Cu KαX-ray). Single-crystal X-ray data were recorded on a Rigaku/XtaLAB P200 MM007HF-DW diffractometer and processed using Rigaku/CrystalClear software. The structure was solved by direct methods (Sir 2004) and refined by full-matrix least-squares refinement using the SHELXL-2013 computer program. The hydrogen atoms were refined geometrically by using a riding model. TGA curves were generated by a thermal analyzer (Seiko Instruments, EXSTAR 6000) at scan rate 5 K/min. Adsorption isotherms were measured with BELSORP-max volumetric adsorption equipment. Elemental analyses (C,H,N) were carried out on a J-SCIENCE LAB JM10 analyser at the Instrumental Analysis Centre of Kumamoto University.

Table S1 Crystal Parameters for **1·2H_2O** and **2·MeOH**

	1·2H$_2$O	**2·MeOH**
Formula	C20 H14 Cl2 Co N4 O2	C21 H18 Br2 Co N4 O
Formula weight	474.21	561.14
Temperature / K	100	100
Crystal System	monoclinic	monoclinic
Space Group	P 2/n (#13)	P 2$_1$/c (#14)
a / Å	8.8298 (6)	8.5932 (7)
b / Å	11.2957 (8)	10.7755 (8)
c / Å	10.6572 (7)	21.7683 (18)
α / deg	90.0000	90.0000
β / deg	112.828 (9)	97.685 (13)
γ / deg	90.0000	90.0000
V / Å^3	979.68	1997.55
Z values	2	4
R - Factor	3.44	9.56

Table S2 Selected Bond Lengths and Angles for **1·2H$_2$O**

Bond Length (Å)			
Co-N(1)	2.173(2)		
Co-N(2)	2.079(2)		
Co-N(3)	2.142(2)		
Bond Angle (deg)			
N(1)-Co-N(1)	151.66(9)	N(1)-Co-Cl(1)	88.61(6)
N(1)-Co-N(2)	75.83(9)	N(2)-Co-Cl(1)	90.67(7)
N(1)-Co-N(3)	104.17(9)	N(3)-Co-Cl(1)	89.33(6)

Table S3 Selected Bond Lengths and Angles for **2·MeOH**

Bond Length (Å)			
Co-N(1)	2.009(9)	Co-N(4)	1.982(9)
Co-N(2)	1.865(9)		
Co-N(3)	1.975(9)		
Bond Angle (deg)			
N(1)-Co-N(2)	80.6(4)	N(2)-Co-Br(1)	86.5(3)
N(1)-Co-N(3)	163.1(4)	N(3)-Co-Br(1)	84.2(3)
N(1)-Co-N(4)	99.1(4)	N(4)-Co-Br(1)	93.3(3)
N(2)-Co-N(3)	82.6(4)	N(1)-Co-Br(2)	88.0(3)
N(2)-Co-N(4)	179.6(4)	N(2)-Co-Br(2)	86.6(3)
N(3)-Co-N(4)	97.7(4)	N(3)-Co-Br(2)	91.4(3)
N(1)-Co-Br(1)	94.4(3)	N(4)-Co-Br(2)	93.5(3)

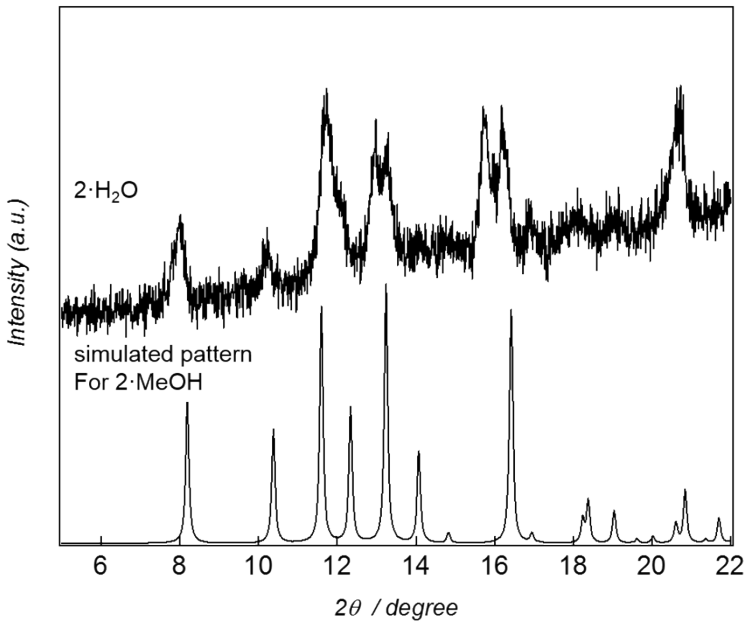

Figure S1 XRPD for **2·MeOH** and **2·H_2O**

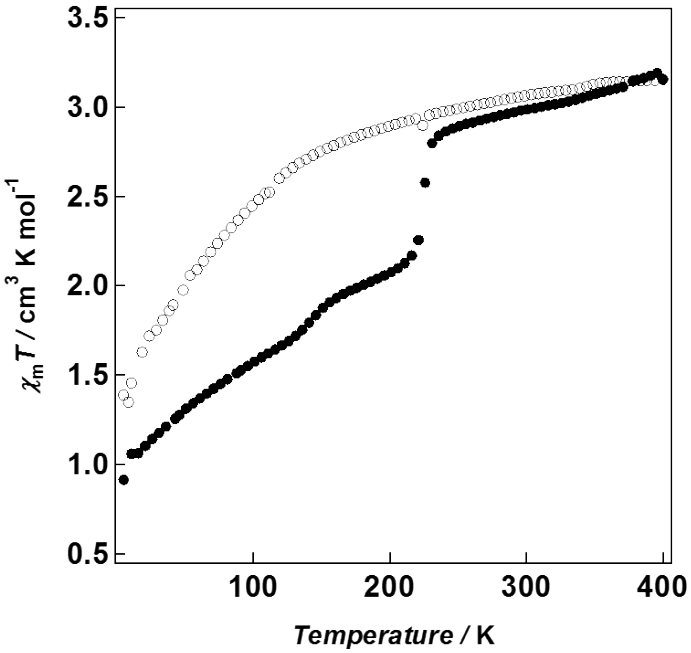

Figure S2 Magnetic properties for **1·2H_2O** (filled circle) and its desolvated compound **1** (open circle).