

Supporting Information

Microwave-assisted synthesis: from a mononuclear $\{\text{Co}^{\text{II}}\}$ complex to $\{\text{Co}^{\text{II}}\}_9$ solvomorphs.

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1. Experimental section and physical measurements

Solvothermal conditions

Mixture of complexes: $[\text{Co}^{\text{II}}(\text{H}_2\text{bic})\text{Cl}]$ (**1**), $[\text{Co}^{\text{II}}_9(\text{Hbic})_4(\text{bic})_2\text{Cl}_4]$ (**2**) and $[\text{Co}^{\text{II}}_9(\text{Hbic})_4(\text{bic})_2\text{Cl}_4] \cdot 12\text{H}_2\text{O}$ (**2**·12H₂O)

Into a solution of bicine (H₃bic, *N,N*-Bis(2-hydroxyethyl)glycine) (0.5 mmol, 82 mg) in EtOH (2 ml) was added a solution of CoCl₂·6H₂O (1 mmol, 238 mg) in EtOH (5 ml) and the solution was stirred for 5 minutes at room temperature. Then, NEt₃ (0.13 mmol, 0.02 ml) was added and the solution stirred for another 15 minutes. The dark blue solution was placed in a Teflon lined autoclave and heated to 140 °C, at a rate of 5 °C/min. The temperature was held at 140 °C for 3 days and then the solution was allowed to cool to room temperature at a rate of 0.1 °C/min yielding three kinds of crystals: pink and blue block-like crystals and blue needle-like crystals.

Single-crystal X-ray diffraction revealed that the unit cell of the pink block-like crystals corresponds to the previously reported $[\text{Co}^{\text{II}}(\text{H}_2\text{bic})\text{Cl}]$ (**1**)¹ and the blue block-like crystals correspond to complex $[\text{Co}^{\text{II}}_9(\text{Hbic})_4(\text{bic})_2\text{Cl}_4]$ (**2**). Single-crystal X-ray diffraction for the blue needle-like crystals revealed a solvomorph of **2**, complex $[\text{Co}^{\text{II}}_9(\text{Hbic})_4(\text{bic})_2\text{Cl}_4] \cdot 12\text{H}_2\text{O}$ (**2**·12H₂O).

Microwave-mediated conditions

Microwave reactor model: Discover LabMate (model no. 908010), Matthews. NC, made in USA by CEM Corporation.

$[\text{Co}^{\text{II}}(\text{H}_2\text{bic})\text{Cl}]$ (1**)**

A solution of CoCl₂·6H₂O (1 mmol, 238 mg), bicine (0.5 mmol, 82 mg) and NEt₃ (0.13 mmol, 0.02 ml) in EtOH (7 ml) was placed in a glass tube sealed with a cap (suitable glass tube and cap designed for microwave reaction), which was then inserted into the cavity of a microwave reactor. The reaction mixture was held at 140 °C, power: 150 W and pressure: 300 PSI for a total of 15 min. Then the solution was allowed to cool naturally to room temperature to give a dark blue solution with pink crystalline precipitate which was collected by filtration and dried in air before characterising with powder X-ray diffraction and elemental analysis (~18% yield). Elemental analysis calcd(%) for C₆H_{12.5}CoNO_{4.25}Cl: C 27.61%, H 4.83%, N 5.37%, found: C 27.49%, H 4.69%, N 5.26%, which corresponds to $[\text{Co}^{\text{II}}(\text{H}_2\text{bic})\text{Cl}] \cdot 0.25\text{H}_2\text{O}$ (**1**·0.25H₂O).

$[\text{Co}^{\text{II}}_9(\text{Hbic})_4(\text{bic})_2\text{Cl}_4]$ (2**)**

A solution of CoCl₂·6H₂O (1 mmol, 238 mg), bicine (0.5 mmol, 82 mg) and NEt₃ (0.5 mmol, 0.075 ml) in EtOH (7 ml) was placed in a sealed glass tube, which was then inserted into the cavity of a microwave reactor. The reaction mixture was held at 140 °C, power: 150 W and pressure: 300 PSI for a total of 15 min. Then the solution was allowed to cool naturally to room temperature to give a dark blue solution with blue crystalline precipitate which was collected by filtration and dried under a nitrogen atmosphere before characterising with powder X-ray diffraction and elemental analysis (~17% yield). Elemental analysis calcd(%) for C₃₆H₆₄Co₉N₆O₂₄Cl₄: C 26.41%, H 3.94%, N 5.13%, found: C 26.27%, H 4.12%, N 4.91%.

[Co^{II}₉(Hbic)₄(bic)₂Cl₄]-12H₂O (2·12H₂O)

A solution of CoCl₂·6H₂O (1 mmol, 238 mg), bicine (0.5 mmol, 82 mg) and NEt₃ (0.5 mmol, 0.075 ml) in EtOH (7 ml) was placed in a sealed glass tube, which was then inserted into the cavity of a microwave reactor. The reaction mixture was held at 140 °C, power: 150 W and pressure: 300 PSI for a total of 15 min. Then the solution was allowed to cool naturally to room temperature to give a dark blue solution with blue crystalline precipitate which was collected by filtration and dried in air before characterising with powder X-ray diffraction and elemental analysis (~17% yield). Elemental analysis calcd(%) for C₃₆H₈₆Co₉N₆O₃₅Cl₄: C 23.56%, H 4.72%, N 4.58%, found: C 24.06%, H 4.39%, N 4.52% which corresponds to [Co^{II}₉(Hbic)₄(bic)₂Cl₄]-11H₂O (one molecule of water is lost).

Single-Crystal X-ray Diffraction: Crystallographic data were collected at 100 K using Mo – K_α radiation (λ = 0.710735 Å) using a Rigaku FRE+ equipped with VHF Varimax confocal mirrors and an AFC12 goniometer and HG Saturn 724+ detector.

Powder X-Ray Diffraction (PXRD): PXRD measurements were carried out at 298 K using a PANalytical X'Pert PRO diffractometer (λ (CuKα) = 1.4505 Å) on a mounted bracket sample stage over the range of 3° < 2θ < 40° (for complex **1**) and 3° < 2θ < 30° (for complexes **2** and **2**·12H₂O) using a step size of 0.0334°.

Magnetic Susceptibility Measurements: Variable-temperature direct current (dc) and alternating current (ac) magnetic susceptibility data were collected on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 5 T magnet operating in the 290 - 2 K range. Polycrystalline samples were embedded in eicosane, to prevent torquing. Magnetic data have been corrected for diamagnetism (Pascal's constants and corrections for the sample holder).

Microanalysis: Elemental analyses (C, H, and N) were performed in-house in the School of Chemistry at the University of Glasgow.

2. Single-Crystal X-ray Diffraction

Due to a region of poorly defined and disordered molecules of solvent in **2**·12H₂O, only two molecules of water were able to be modelled. The programme SQUEEZE (in PLATON) ² was used to identify the solvent voids and account for the electron density within them, calculated to contain 886 e⁻ per unit cell, corresponding to approximately 98 e⁻ per molecule. Approximately 10 molecules of water solvent correspond to ~98 e⁻, therefore in total there are 12 molecules of co-crystallised water per complex. This is also in agreement with the elemental analysis (see experimental procedure of [Co^{II}₉(Hbic)₄(bic)₂Cl₄]-12H₂O (**2**·12H₂O)).

Solvent Accessible Volume = 3665 Å³

Electrons Found in S.A.V. = 886

Data collection: CrysAlisPro 1.171.39.9g (Rigaku Oxford Diffraction, 2015); cell refinement: CrysAlisPro 1.171.39.9g (Rigaku Oxford Diffraction, 2015); data reduction: CrysAlisPro 1.171.39.9g (Rigaku Oxford Diffraction, 2015); program used to solve structure: ShelXT; ³ program used to refine structure: SHELXL; ³ molecular graphics: Olex2; ⁴ software used to prepare material for publication: Olex2. ⁴

Table S1. Data collection and crystallographic parameters for complexes **2** and **2·12H₂O**.

Chemical formula	C ₃₆ H ₆₄ Cl ₄ Co ₉ N ₆ O ₂₄ (2)	C ₃₆ H ₈₈ Cl ₄ Co ₉ N ₆ O ₃₆ (2·12H₂O)
M_r	1637.10	1853.29
Crystal system, space group	Monoclinic, <i>P2₁/n</i>	Trigonal, <i>R</i> -3
Temperature (K)	100	100
a, b, c (Å)	14.7276 (4), 11.8295 (3), 15.6451 (5)	39.2116 (8), 39.2116 (8), 11.7240 (3)
α, β, γ (°)	90, 94.809, 90	90, 90, 120
V (Å³)	2716.10 (13)	15611.2 (8)
Z	2	9
Radiation type	Mo Kα radiation, λ = 0.71073 Å	Mo Kα radiation, λ = 0.71073 Å
μ (mm⁻¹)	2.96	2.34
Crystal size (mm)	0.08 × 0.07 × 0.04	0.26 × 0.03 × 0.03
Diffractometer	Rigaku FRE+ equipped with VHF Varimax confocal mirrors and an AFC12 goniometer and HG Saturn 724+ detector diffractometer	Rigaku FRE+ equipped with VHF Varimax confocal mirrors and an AFC12 goniometer and HG Saturn 724+ detector diffractometer
T_{min}, T_{max}	0.874, 1.000	0.555, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	34254, 6234, 5718	38042, 7930, 6410
R_{int}	0.028	0.061
R[F² > 2σ(F²)], wR(F²), S	0.023, 0.055, 1.03	0.054, 0.139, 1.00
No. of reflections	6234	7930
No. of parameters	364	368
No. of restraints	6	483
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
Δ>max, Δ>min (e Å⁻³)	1.25, -0.66	2.11, -1.63

Table S2. The CShMs values calculated with the program SHAPE⁵ for each geometry for the five-coordinate Co^{II} in complex **1**.

Geometry	Value
Pentagon	34.70
Vacant octahedron	6.75
Trigonal bipyramid	1.42
Spherical square pyramid	5.53
Johnson trigonal bipyramid	2.63

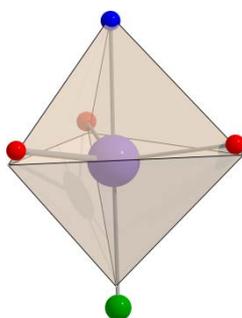


Figure S1. The closest reference polyhedron for TBP geometry calculated with SHAPE⁵ for Co^{II} of complex **1**. Colour code: Co^{II}: violet, Cl: green, O: red, N: blue, bonds: grey.

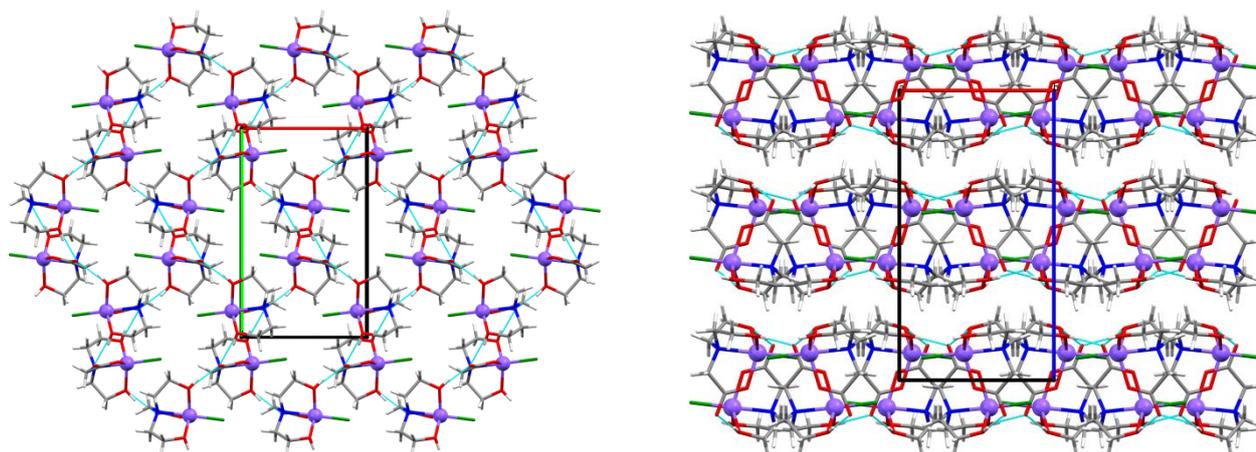


Figure S2. *Left:* The crystal packing of **1** along the *c* axis. *Right:* The crystal packing of **1** along the *b* axis. Colour code: Co^{II}: violet, Cl: green, O: red, N: blue, C: grey, H: white. Light blue lines: illustration of the 2D network formed by the H-bonds.

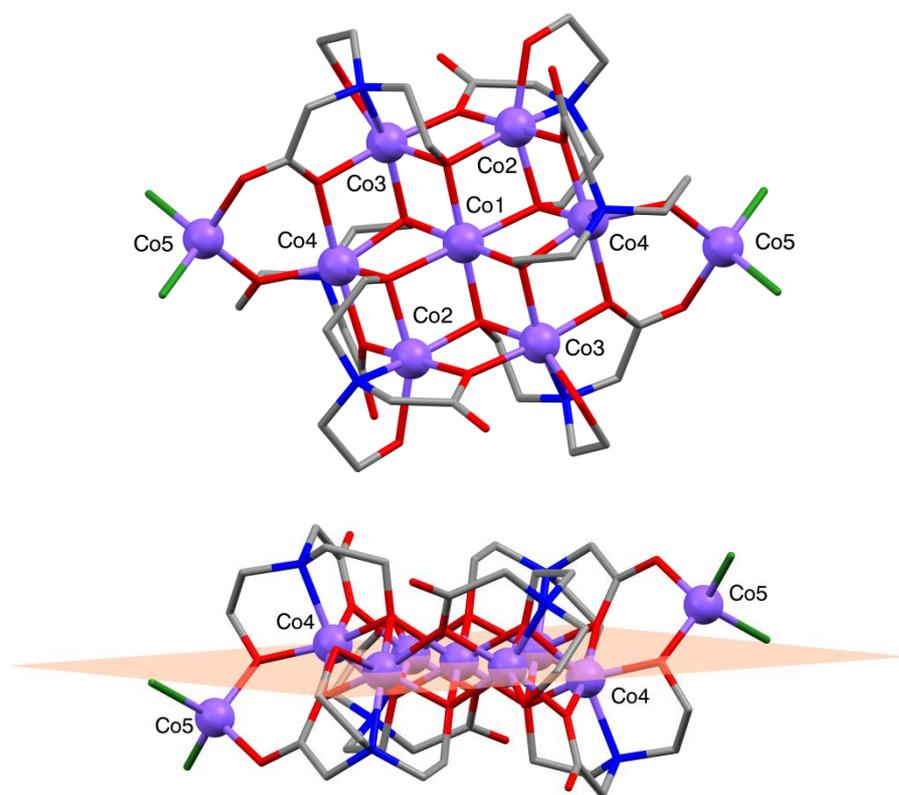


Figure S3. *Top:* The molecular structure of [Co^{II}₉(Hbic)₄(bic)₂Cl₄]. *Bottom:* The plane that five Co^{II} (Co1, Co2, Co2', Co3, Co3') centres define, with Co4, Co4', Co5 and Co5' located outside this plane. Colour code: Co^{II}: violet, Cl: green, O: red, N: blue, C: grey. Hydrogen atoms are omitted for clarity.

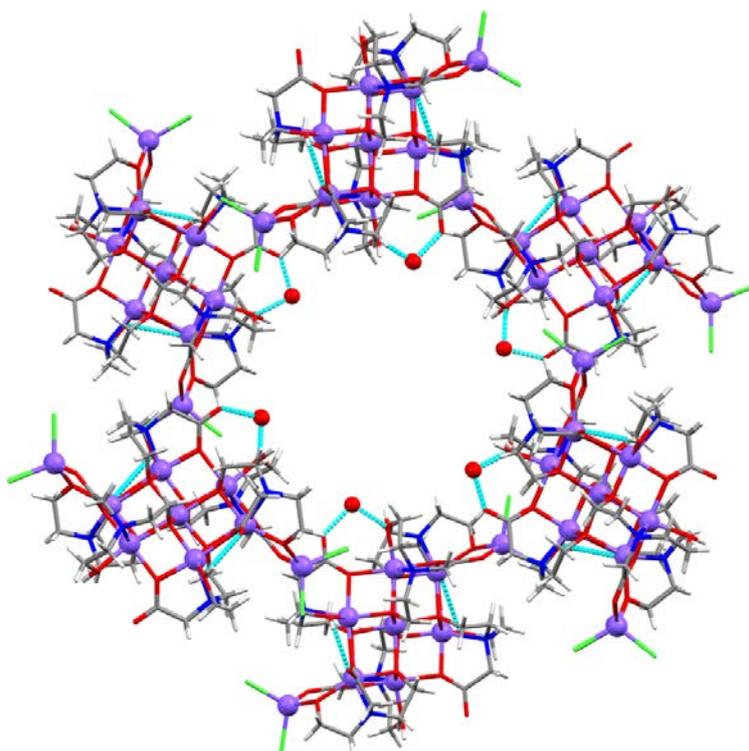


Figure S4. Illustration of the intramolecular and intermolecular interactions through the hydrogen bonds (light blue dashed lines) for complex **2**·12H₂O. Only the modelled H₂O sites are shown here, however further water molecules are present in the channels and were accounted for using SQUEEZE.⁶

Table S3. The CShMs values calculated with the program SHAPE⁷ for each Co^{II} centre in complex **2**.

Co	Octahedron	Trigonal prism	Tetrahedron
Co1	1.3	-	-
Co2	3.3	-	-
Co3	4.5	5.3	-
Co4	4.8	5.4	-
Co5	-	-	0.8

Table S4. The CShMs values calculated with the program SHAPE ⁷ for each Co^{II} centre in complex **2**·12H₂O.

Co	Octahedron	Trigonal prism	Tetrahedron
Co1	1.3	-	-
Co2	3.7	-	-
Co3	3.8	-	-
Co4	4.7	5.3	-
Co5	-	-	0.7

3. Dc and ac magnetic susceptibility

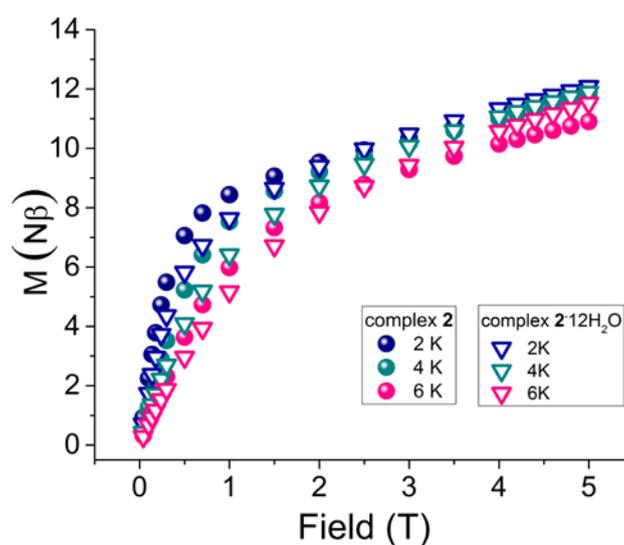


Figure S5. Magnetisation versus Field plot at temperatures 2, 4 and 6 K for complexes **2** (spheres) and **2**·12H₂O (triangles).

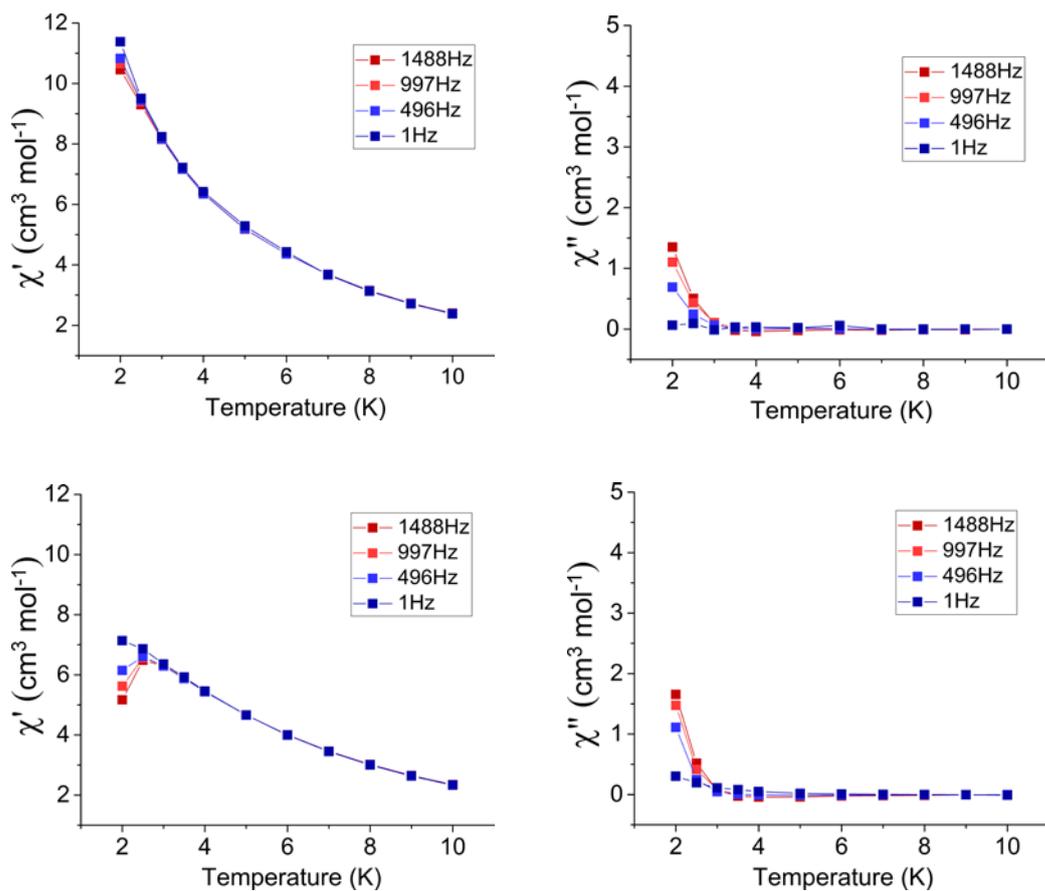


Figure S6. *Top:* Temperature dependence of the in-phase (*left*) and out-of-phase (*right*) susceptibility in zero dc field for complex **2** with ac frequencies of 1–1488 Hz. *Bottom:* Temperature dependence of the in-phase (*left*) and out-of-phase (*right*) susceptibility in a 2000 Oe dc field for complex **2** with ac frequencies of 1–1488 Hz. Note that the optimum additional dc field was not determined.

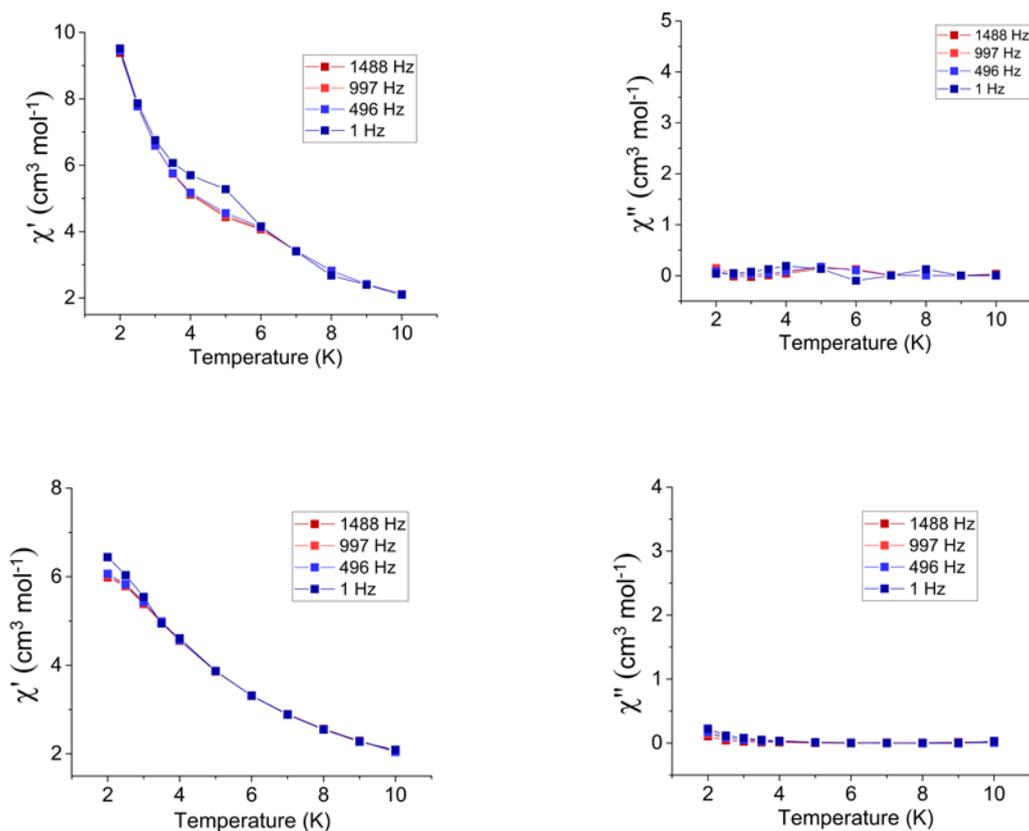


Figure S7. *Top:* Temperature dependence of the in-phase (*left*) and out-of-phase (*right*) susceptibility in zero dc field for complex **2**·12H₂O with ac frequencies of 1–1488 Hz. *Bottom:* Temperature dependence of the in-phase (*left*) and out-of-phase (*right*) susceptibility in a 2000 Oe dc field for complex **2**·12H₂O with ac frequencies of 1–1488 Hz.

4. References

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