

Spin State Modulation and Kinetic Control of Thermal Contraction in a [Fe₂Co₂] Discrete Prussian Blue Analogue

Jyoti Yadav^[a] and Sanjit Konar^{*[a]}

[a] Jyoti Yadav and Sanjit Konar*
Department of Chemistry, Elements Building
Indian Institute of Science Education and Research Bhopal
Bhauri, Bhopal By-pass road, Madhya Pradesh, India- 462066
E-mail: jyoti17@iiserb.ac.in, skonar@iiserb.ac.in

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Experimental Procedures

1.1. Materials:

Cobalt (II) perchlorate hexahydrate and Ferric chloride were purchased from Merck and used as received. All other chemicals Potassium tris(1-Pyrazolyl) borohydride, 2-Cyanopyridine, Aniline, and Sodium Methoxide were bought from Sigma- Aldrich. Sodium Cyanide is from Loba Chemie. All the reactions were performed under ambient atmospheric conditions.

Caution! Cyanides are highly toxic, therefore, they should be handled with great care and precautions. The unreacted cyanides and the glassware used for the cyanide reaction were quenched by an aqueous solution of KMnO_4 . Since perchlorates are highly explosive, heating was done carefully, if required.

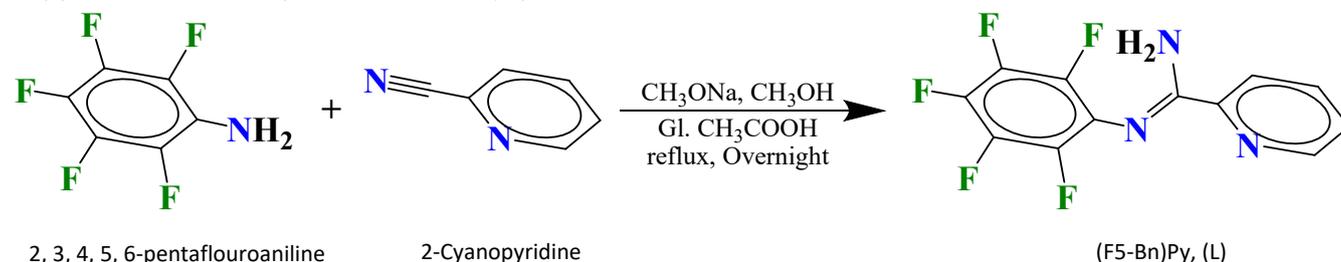
1.2. Synthetic procedures:

1.2.1. Synthesis of $\text{Na}[\text{Fe}(\text{Tp})(\text{CN})_3]$:

The Fe-CN complex was prepared according to the earlier procedure reported.¹ Instead of KCN, NaCN was used. IR: $\nu_{\text{CN}} = 2126 \text{ cm}^{-1}$

1.2.2. Synthesis of ligand ((F5-Bn)Py), (L):

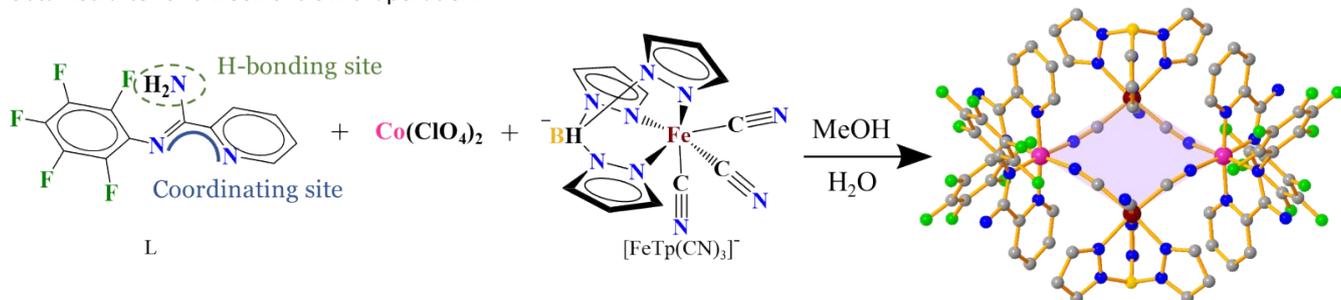
A suspension of 20 ml MeOH and 250 mg of NaOMe was taken in a 50 ml round bottom flask and stirred for 10 minutes. 2-Cyanopyridine (5 mmol) was added to the suspension and heated for 30 minutes. 2, 3, 4, 5, 6-pentafluoroaniline (5 mmol) was added to the reaction mixture and refluxed overnight. The solution was evaporated to dryness and washed with diethyl ether. After evaporation, the diethyl ether part gives a colourless crystal of the ligand (L). IR: $\nu_{\text{NH}} = 3405, 3316, 3272 \text{ cm}^{-1}$, $\nu_{\text{CH}} = 3210, 3179 \text{ cm}^{-1}$, $\nu_{\text{C-C}} = 1592, 1568 \text{ cm}^{-1}$, $\nu_{\text{C-N}} = 1655, 1643 \text{ cm}^{-1}$, $\nu_{\text{C-F}} = 1498 \text{ cm}^{-1}$.



Scheme S1. Synthesis of ligand ((F5-Bn)Py), (L).

1.2.3. Synthesis of $[\text{Fe}(\text{Tp})(\text{CN})_3]_2[\text{Co}\{\text{L}\}]_2(\text{ClO}_4)_2 \cdot 4\text{MeOH} \cdot 2\text{H}_2\text{O}$ (1·4MeOH·2H₂O):

Methanolic solution of ligand and $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ was added to a 2: 1 MeOH: H₂O solution of $\text{Na}[\text{FeTp}(\text{CN})_3]$ and heated at 40 °C for 30 minutes. The solution was filtered hot and kept for crystallisation. Red plate-like crystals of complex 1·4MeOH·2H₂O were obtained after one week of slow evaporation.



Scheme S2. Synthesis of $[\text{Fe}(\text{Tp})(\text{CN})_3]_2[\text{Co}\{\text{L}\}]_2(\text{ClO}_4)_2 \cdot 4\text{MeOH} \cdot 2\text{H}_2\text{O}$ (1·4MeOH·2H₂O).

Elemental Analysis: 1·4MeOH·2H₂O: Experimental: N = 18.48%, C = 40.17% and H = 2.92%; Calculated: C = 39.39%, H = 2.52% and N = 18.13%.

1.2.4. Partially desolvated complex (1·2H₂O):

The complex was obtained by the eventual escape of methanol molecules when kept at room temperature (25° C). The bulk sample was prepared by keeping the crystals under vacuum for 2-3 hours at room temperature. Selective loss of methanol molecules was observed.

Elemental Analysis: 1·2H₂O: Experimental: C = 39.79%, H = 2.36%, N = 19.63%; Calculated: C = 39.39%, H = 2.20%, N = 19.14%.

1.2.5. Desolvated Complex (1):

The desolvation process was done by keeping freshly prepared samples at 50°C under a high vacuum for ~1 hour. The complete loss of solvents was characterised by elemental analysis and infrared spectroscopy.

Elemental Analysis: 1: Experimental: C = 40.38%, H = 2.32%, N = 19.32%; Calculated: C = 40.05%, H = 2.05%, N = 19.46%.

1.3. Physical measurements:

1.3.1. Crystal Data Collection and Structure Determination:

Intensity data were collected on a 'Bruker D8-Quest' diffractometer using a graphite monochromated MoK α radiation ($\lambda = 0.71073$) at 140 K. Data collections were performed using ϕ and ω scan. Olex2 was used as the graphical interface and the structures were solved with olex2.solve structure solution program using Charge Flipping and refined with the ShelXL refinement package using Least-Squares minimisation. All non-hydrogen atoms were refined anisotropically.² Shape analysis was done by continuous shape measurement (CShM) program and octahedral distortion parameters were calculated by using the software "Octadist".³

1.3.2. Squid Magnetometry Study:

The magnetic study has been performed using a SQUID-VSM magnetometer. All samples were ground properly before measuring magnetic moment vs. temperature data, to minimize the reorientation of the crystalline particles under the applied DC field. All the measurements have been performed with an applied DC field of 10000 Oe and 1000 Oe from the 2 K to 300 K temperature range. The measured values were corrected for the experimentally measured contribution of the sample holder and the derived susceptibilities were corrected for the diamagnetism of the samples, estimated from Pascal's tables.

The photomagnetic study was performed using a SQUID magnetometer integrated with a fibre optic sample holder (FOSH). A thin layer of 3.3 mg sample was spread evenly on a transparent tape and inserted into the optic fibre holder. The sample was irradiated with light of different wavelengths ranging from 436 nm to 850 nm at 10 K and showed maximum conversion with 525 nm of light. The sample was irradiated for 1 hour at each of the wavelengths to check for the generation of the metastable state. For the wavelengths accelerating the conversion of the diamagnetic sample to the metastable state, the irradiation was done up to saturation to the excited state, which was approximately 4-5 hours. The photo-irradiation was followed by the thermal treatment of the sample in dark conditions and observed for the temperature of relaxation to its diamagnetic state.

The operating pressure range of the hydrostatic pressure cell, which is composed of hardened beryllium bronze and uses low-viscosity Daphne oil as the pressure-transferring medium, is 10⁵ Pa to 1.3 GPa. The sample holders for the powder were cylindrical, measuring 1.1 mm in diameter and 5 mm in length. The built-in pressure sensor composed of highly pure Pb was used to measure the pressure utilizing the pressure dependence of the superconducting transition temperature. The mentioned applied pressures are the approximate calculated values concerning the compression of the Teflon tube consisting of sample, Pb and the pressure-transferring medium.

1.3.3. Thermogravimetric Analysis:

The Thermogravimetric analysis was performed on a PerkinElmer instrument at a scan rate of 3 K/min.

1.3.4. FT-Infrared Spectroscopy:

FT-IR spectra were recorded by using a Perkin-Elmer Spectrum BX Spectrometer with a wavenumber ranging between 4000 cm⁻¹ - 400 cm⁻¹.

Results and Discussion

2.1. Crystal structure determination of 1·4MeOH·2H₂O:

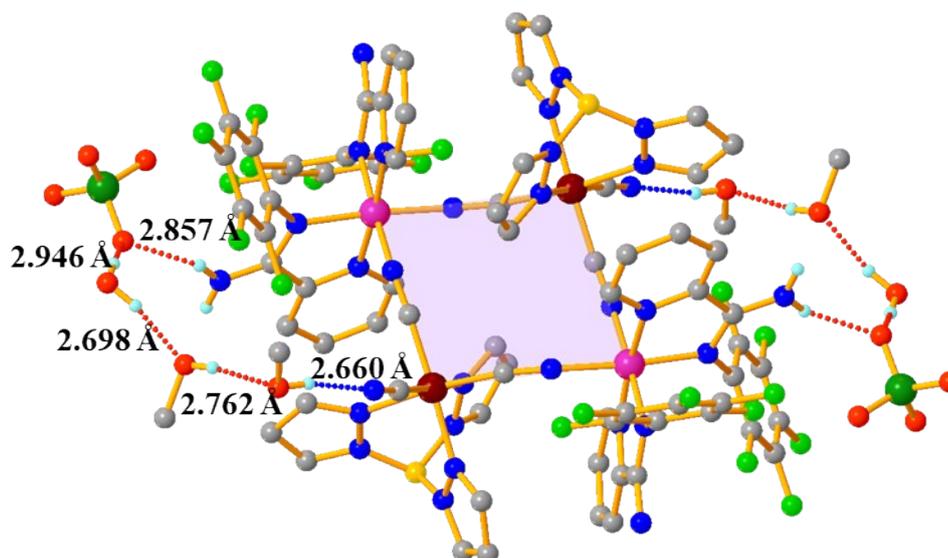


Figure S1. Crystal Structure of 1·4MeOH·2H₂O. Colour Code: Green: Fe; Pink: Co; Blue: N; Grey: C; Yellow: B, Dark green: Cl, Light green: F. H-bonding interactions between the square complex, solvents and anions are shown with red dotted lines. The hydrogen not involved in H-bonding is omitted for clarity.

Table S1. Crystallographic data of 1·4MeOH·2H₂O:

Identification code	1·4MeOH·2H ₂ O			
Temperature (K)	100	168	200	250
Empirical formula	C ₃₈ H ₂₉ BClCoF ₁₀ FeN ₁₅ O ₇	C ₃₈ H ₂₉ BClCoF ₁₀ FeN ₁₅ O ₇	C ₃₈ H ₂₉ BClCoF ₁₀ FeN ₁₅ O ₇	C ₃₈ H ₃₂ BClCoF ₁₀ FeN ₁₅ O ₇
Formula weight	1158.80	1158.80	1158.80	1161.82
Temperature/K	100.0	168.0	200.0	250.0
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
a/Å	14.735(5)	14.852(5)	14.867(4)	14.938(11)
b/Å	20.586(7)	20.700(8)	20.702(6)	20.830(16)
c/Å	15.382(6)	15.425(6)	15.437(4)	15.450(12)
α/°	90	90	90	90
β/°	103.396(10)	103.695(11)	103.782(7)	103.72(2)
γ/°	90	90	90	90
Volume/Å ³	4539(3)	4608(3)	4614(2)	4670(6)
Z	4	4	4	4
ρ _{calc} /cm ³	1.696	1.670	1.668	1.652
R ₁ ^a	0.0426	0.0439	0.0432	0.0722
wR ₂ ^a	0.1049	0.1078	0.1103	0.2135
[a] I ≥ 2σ(I): R ₁ = Σ F _o - F _c / Σ F _o , wR ₂ = {Σ[w(F _o - F _c) ²] / Σ[w(F _o) ²]} ^{1/2}				

Table S2. Selected bond lengths of 1·4MeOH·2H₂O:

Atom	Atom	Length/Å			
		100 K	168 K	200 K	250 K
Co1	N15	1.921(3)	1.925(3)	1.922(3)	1.946(7)
Co1	N10	1.914(3)	1.920(3)	1.920(3)	1.942(6)
Co1	N12	1.933(3)	1.939(3)	1.939(3)	1.933(6)
Co1	N13	1.940(3)	1.942(3)	1.942(3)	1.946(7)
Co1	N9	1.890(3)	1.894(3)	1.894(3)	1.899(7)
Co1	N2 ¹	1.909(3)	1.916(3)	1.911(3)	1.906(7)
Fe1	N3	1.999(3)	2.005(3)	2.002(3)	2.005(7)
Fe1	N6	1.996(3)	1.998(3)	1.996(3)	2.017(8)
Fe1	N8	2.007(3)	2.014(3)	2.010(3)	2.000(7)
Fe1	C12	1.857(4)	1.866(4)	1.863(4)	1.878(9)
Fe1	C1	1.889(4)	1.896(4)	1.901(4)	1.883(9)
Fe1	C2	1.866(4)	1.871(4)	1.869(4)	1.900(11)

Table S3. Selected bond angles of 1·4MeOH·2H₂O forming [Fe₂Co₂] square plane:

Atom	Atom	Atom	Angles/°			
			100 K	168 K	200 K	250 K
N9	Co1	N2 ¹	87.52(12)	87.65(12)	87.51(12)	87.5(3)
C12	Fe1	C2	97.36(15)	97.22(15)	97.47(14)	98.1(3)

Table S4. Octahedral Shape Analysis of 1·4MeOH·2H₂O:

Octahedral Shape Analysis Value				
Metal centre	100K	168K	200K	250 K
Co	0.393	0.392	0.401	0.356
Fe	0.187	0.180	0.182	0.186

Table S5. Octahedral distortion parameters for 1·4MeOH·2H₂O:

Temperature	Metal centre	<D> (Å)	Z (Å)	Δ	Σ (°)	Θ (°)
250 K	Co	1.9286	0.105140	0.000099	41.9033	131.3609
	Fe	1.9471	0.361916	0.000978	38.3556	85.1762
100 K	Co	1.9178	0.080549	0.000072	45.2858	138.5380
	Fe	1.9358	0.389730	0.001153	36.2276	85.7889

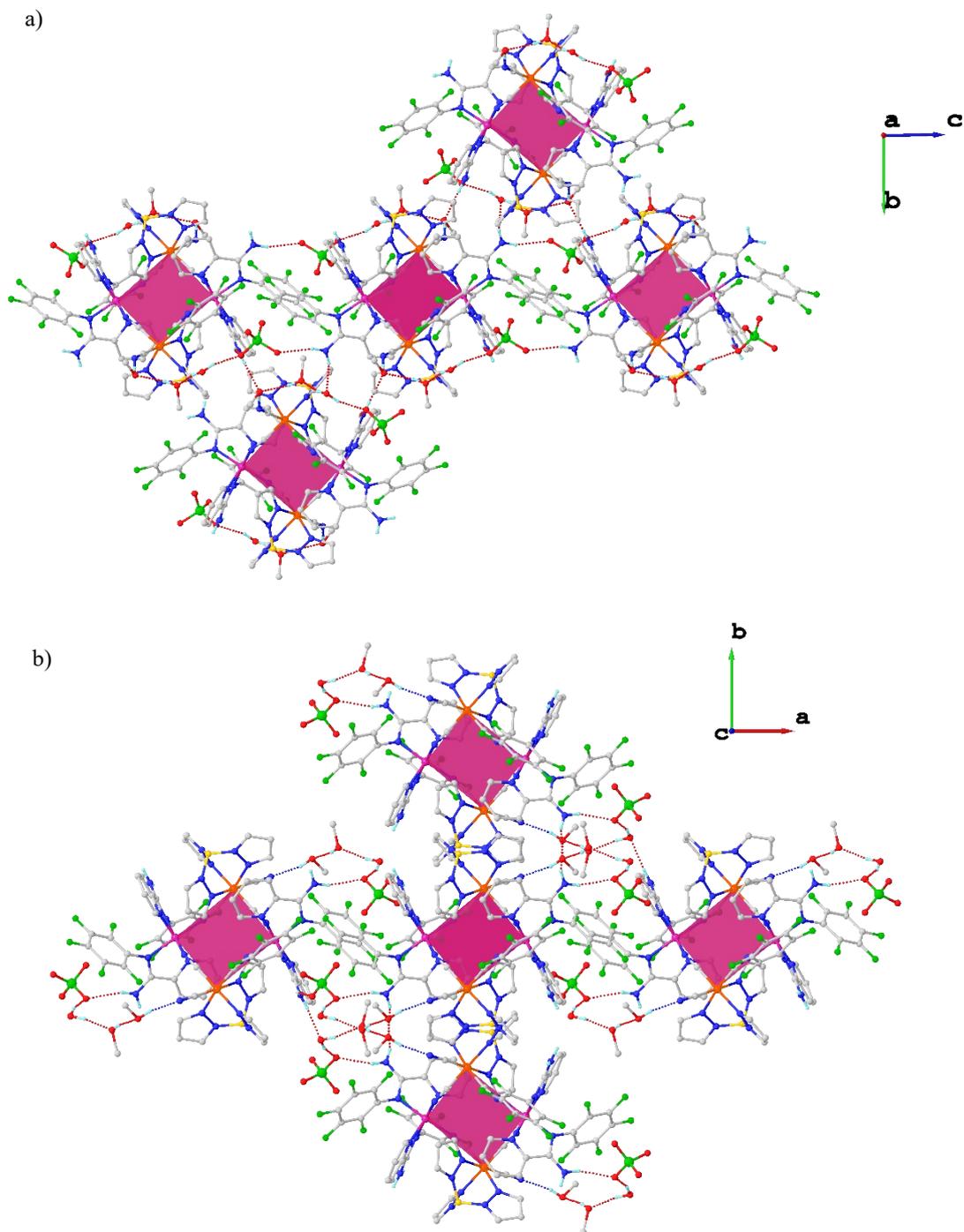


Figure S2. Hydrogen bonding interactions between solvent molecules, perchlorate anions and the $[\text{Fe}_2(\mu\text{-CN})\text{Co}_2]$ square grids a) along the bc plane and b) along the ab plane in complex $1 \cdot 4\text{MeOH} \cdot 2\text{H}_2\text{O}$. The Hydrogen atoms not involved in Hydrogen bonding have been omitted for clarity.

2.2. Crystal structure determination of 1·2H₂O:

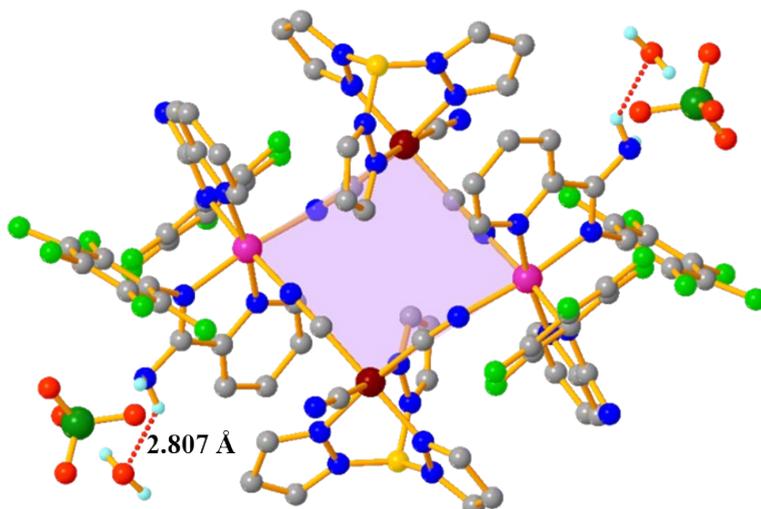


Figure S3. Crystal Structure of 1·2H₂O. Colour Code: Green: Fe; Pink: Co; Blue: N; Grey: C; Yellow: B, Dark green: Cl, Light green: F. H-bonding interactions between the square complex, solvents and anions are shown with red dotted lines. The hydrogen not involved in H-bonding is omitted for clarity.

Table S6. Crystallographic data of 1·2H₂O during cooling @5 K min⁻¹:

Identification code	1_2H ₂ O_200K_1C	1_2H ₂ O_168K_1C	1_2H ₂ O_140K_1C	1_2H ₂ O_110K_1
Temperature (K)	200	168	140	110
Empirical formula	C ₃₆ H ₂₄ BClCoF ₁₀ FeN ₁₅ O ₅	C ₃₆ H ₂₄ BClCoF ₁₀ FeN ₁₅ O ₅	C ₃₆ H ₂₄ BClCoF ₁₀ FeN ₁₅ O ₅	C ₃₆ H ₂₄ BClCoF ₁₀ FeN ₁₅ O ₅
Formula weight	1097.74	1097.74	1097.74	1097.74
Temperature/K	100.0	168.0	140.0	110.0
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
a/Å	14.5189(6)	14.5597(12)	14.5844(15)	14.5659(13)
b/Å	22.4945(8)	22.1504(16)	21.947(2)	21.8912(18)
c/Å	14.6481(6)	14.5863(12)	14.5400(15)	14.5075(14)
α/°	90	90	90	90
β/°	107.3870(10)	107.475(3)	107.574(3)	107.593(3)
γ/°	90	90	90	90
Volume/Å ³	4565.4(3)	4487.0(6)	4436.8(8)	4409.6(7)
Z	4	4	4	4
ρ _{calc} /cm ³	1.597	1.625	1.643	1.654
R ₁ ^a	0.0841	0.0592	0.0573	0.0580
wR ₂ ^a	0.1887	0.1609	0.1555	0.1527
[a] I ≥ 2σ(I): R ₁ = Σ F _o - F _c / Σ F _o , wR ₂ = {Σ[w(F _o - F _c) ²] / Σ[w(F _o) ²]} ^{1/2}				

Table S7. Crystallographic data of 1·2H₂O during heating @5 K min⁻¹:

Identification code	1_2H ₂ O_140K_1H	1_2H ₂ O_168K_1H	1_2H ₂ O_200K_1H
Temperature (K)	140	168	200
Empirical formula	C ₃₆ H ₂₄ BClCoF ₁₀ FeN ₁₅ O ₅	C ₃₆ H ₂₄ BClCoF ₁₀ FeN ₁₅ O ₅	C ₃₆ H ₂₄ BClCoF ₁₀ FeN ₁₅ O ₅
Formula weight	1097.74	1097.74	1097.74
Temperature/K	140.0	168.0	200.0
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
a/Å	14.586(3)	14.555(3)	14.5088(10)
b/Å	21.940(4)	22.133(4)	22.4672(13)
c/Å	14.537(3)	14.590(3)	14.6367(10)
α/°	90	90	90
β/°	107.634(5)	107.506(6)	107.396(2)
γ/°	90	90	90
Volume/Å ³	4433.7(14)	4482.4(17)	4552.9(5)
Z	4	4	4
ρ _{calc} /cm ³	1.645	1.627	1.601
R ₁ ^a	0.0590	0.0583	0.0816
wR ₂ ^a	0.1547	0.1594	0.1888
[a] I ≥ 2σ(I): R ₁ = Σ F _o - F _c / Σ F _o , wR ₂ = {Σ[w(F _o - F _c) ²] / Σ[w(F _o) ²]} ^{1/2}			

Table S8. Selected bond lengths of 1·2H₂O during cooling and heating mode @5 K min⁻¹:

Atom	Atom	Bond length/Å						
		200	168	140	110	140	168	200
Co1	N13	2.110(6)	2.061(4)	2.008(4)	2.005(4)	2.014(4)	2.062(4)	2.124(6)
Co1	N12	2.113(6)	2.047(4)	2.012(4)	2.002(4)	2.012(4)	2.048(4)	2.108(5)
Co1	N15	2.109(5)	2.052(4)	1.997(4)	1.998(4)	2.001(4)	2.047(4)	2.112(6)
Co1	N2 ¹	2.107(6)	2.032(4)	1.989(4)	1.983(4)	1.989(4)	2.031(4)	2.099(6)
Co1	N9	2.107(6)	2.028(4)	1.976(4)	1.974(4)	1.981(4)	2.024(4)	2.106(6)
Co1	N10	2.129(6)	2.041(4)	2.024(4)	2.015(4)	2.025(4)	2.039(4)	2.110(6)
Fe1	N3	1.975(6)	1.981(4)	1.988(4)	1.990(4)	1.987(4)	1.979(4)	1.969(6)
Fe1	N8	1.968(6)	1.991(4)	1.984(4)	1.986(4)	1.983(4)	1.987(4)	1.967(6)
Fe1	N6	1.975(6)	1.980(4)	1.994(4)	1.996(4)	2.001(4)	1.978(4)	1.970(6)
Fe1	C12	1.913(8)	1.896(5)	1.893(5)	1.885(5)	1.881(5)	1.900(5)	1.895(7)
Fe1	C2	1.894(7)	1.885(5)	1.880(5)	1.871(5)	1.869(5)	1.885(5)	1.925(8)
Fe1	C1	1.924(8)	1.918(5)	1.922(5)	1.917(5)	1.913(5)	1.918(5)	1.923(7)

Table S9. Selected bond angles of 1·2H₂O during cooling and heating mode @5 K min⁻¹:

Atoms			Angles/°						
			200 K	168 K	140 K	110 K	140 K	168 K	200 K
N9	Co1	N2 ¹	84.9(2)	85.10(15)	85.53(15)	85.85(15)	85.71(15)	85.31(15)	84.7(2)
C12	Fe1	C2	90.6(3)	93.24(19)	94.70(19)	94.70(19)	94.64(19)	93.28(19)	90.8(3)

Table S10. Octahedral Shape Analysis of 1·2H₂O during cooling and heating mode @5 K min⁻¹:

Octahedral Shape Analysis Value							
Metal centre	200 K	168 K	140 K	110 K	140 K	168 K	200 K
Co	1.130	0.883	0.723	0.723	0.706	0.869	1.150
Fe	0.109	0.147	0.167	0.167	0.166	0.135	0.105

Table S11. Octahedral distortion parameters for 1·2H₂O during cooling and heating mode @5 K min⁻¹:

Temperature (K)	Metal centre	<D> (Å)	Z (Å)	Δ	Σ (°)	Θ (°)
200	Co	2.1125	0.034745	0.000013	71.3885	216.0295
	Fe	1.9415	0.186854	0.000278	21.0018	64.1777
168	Co	2.0435	0.058561	0.000030	62.7426	197.4726
	Fe	1.9420	0.252804	0.000499	24.7315	77.3182
140	Co	2.0012	0.081449	0.000061	56.5163	181.0988
	Fe	1.9433	0.271347	0.000586	26.9007	83.3626
110	Co	1.9965	0.070066	0.000047	54.6728	175.5133
	Fe	1.9407	0.298537	0.000708	26.0526	82.7088
140	Co	2.0037	0.079822	0.000057	55.7630	178.6307
	Fe	1.9389	0.309204	0.000761	26.1240	82.5078
168	Co	2.0417	0.063576	0.000037	61.9579	195.7921
	Fe	1.9413	0.240597	0.000453	24.2697	74.3951
200	Co	2.1099	0.032355	0.000012	71.8219	218.3610
	Fe	1.9417	0.163342	0.000221	21.3293	64.4477

Table S12. Crystallographic data of 1·2H₂O during heating @1 K min⁻¹:

Identification code	1_2H ₂ O_120K_2H	1_2H ₂ O_140K_2H	1_2H ₂ O_168K_2H	1_2H ₂ O_200K_2H
Temperature (K)	120	140	168	200
Empirical formula	C ₃₆ H ₂₄ BClCoF ₁₀ FeN ₁₅ O ₅	C ₃₆ H ₂₄ BClCoF ₁₀ FeN ₁₅ O ₅	C ₃₆ H ₂₄ BClCoF ₁₀ FeN ₁₅ O ₅	C ₃₆ H ₂₄ BClCoF ₁₀ FeN ₁₅ O ₅
Formula weight	1097.74	1097.74	1097.74	1097.74
Temperature/K	120.0	140.0	168.0	200.0
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
a/Å	14.608(3)	14.6328(10)	14.618(3)	14.5568(5)
b/Å	21.690(4)	21.6526(17)	21.998(4)	22.4909(8)
c/Å	14.447(3)	14.4816(12)	14.513(3)	14.6069(5)
α/°	90	90	90	90
β/°	107.574(4)	107.596(4)	107.492(4)	107.3370(10)
γ/°	90	90	90	90
Volume/Å ³	4363.8(14)	4373.6(6)	4451.1(15)	4565.0(3)
Z	4	4	4	4
ρ _{calc} /cm ³	1.671	1.667	1.638	1.597
R ₁ ^a	0.0706	0.0918	0.0684	0.1264
wR ₂ ^a	0.1859	0.2086	0.1861	0.2943
[a] I ≥ 2σ(I): R ₁ = Σ F _o - F _c /Σ F _o , wR ₂ = {Σ[w(F _o - F _c) ²]/Σ[w(F _o) ²]} ^{1/2}				

Table S13. Selected bond lengths of 1·2H₂O during heating mode @1 K min⁻¹:

Atom	Atom	Bond length/Å				
		110 K	120 K	140 K	168 K	200 K
Co1	N13	2.005(4)	1.971(5)	1.974(7)	2.030(5)	2.131(9)
Co1	N12	2.002(4)	1.966(5)	1.952(7)	2.030(5)	2.103(9)
Co1	N15	1.998(4)	1.949(6)	1.949(7)	2.020(6)	2.106(9)
Co1	N2 ¹	1.983(4)	1.944(6)	1.933(7)	2.017(5)	2.101(10)
Co1	N9	1.974(4)	1.914(6)	1.913(7)	1.996(6)	2.103(10)
Co1	N10	2.015(4)	1.952(6)	1.960(7)	2.010(5)	2.113(9)
Fe1	N3	1.990(4)	2.001(5)	2.005(7)	1.986(6)	1.953(9)
Fe1	N8	1.986(4)	1.997(5)	1.980(7)	1.990(5)	1.969(9)
Fe1	N6	1.996(4)	1.986(6)	1.995(7)	1.977(5)	1.972(10)
Fe1	C12	1.885(5)	1.874(7)	1.872(9)	1.890(7)	1.875(11)
Fe1	C2	1.871(5)	1.853(7)	1.849(9)	1.871(7)	1.933(13)
Fe1	C1	1.917(5)	1.914(7)	1.908(9)	1.917(7)	1.928(12)

Table S14. Selected bond angles of 1·2H₂O during heating mode @1 K min⁻¹:

Atoms			Angles/°				
			110 K	120 K	140 K	168 K	200 K
N9	Co1	N2 ¹	85.85(15)	86.3(2)	86.7(3)	85.5(2)	85.1(4)
C12	Fe1	C2	94.70(19)	96.1(3)	96.2(3)	93.9(3)	90.4(4)

Table S15. Octahedral Shape Analysis of 1·2H₂O during heating mode @1 K min⁻¹:

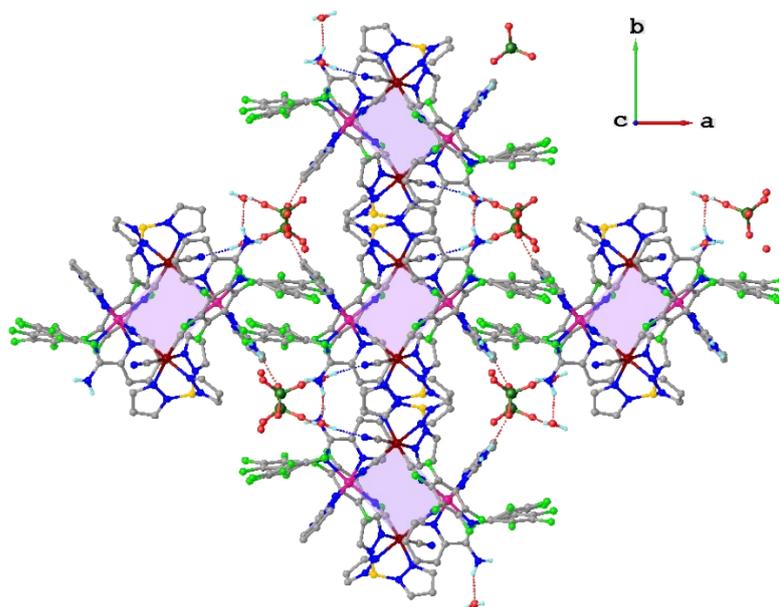
Metal centre	Octahedral Shape Analysis Value				
	110 K	120 K	140 K	168 K	200 K
Co	0.723	0.507	0.499	0.786	1.107
Fe	0.167	0.204	0.213	0.175	0.108

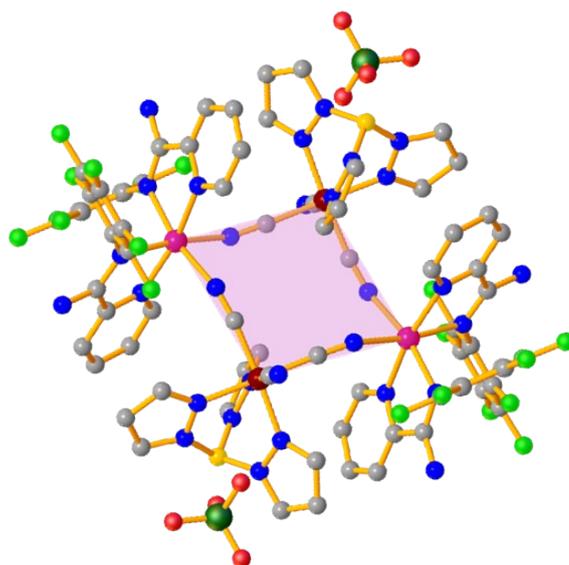
Table S16. Octahedral distortion parameters for 1·2H₂O during cooling and heating mode @1 K min⁻¹:

Temperature (K)	Metal centre	<D> (Å)	Z (Å)	Δ	Σ (°)	Θ (°)
110	Co	1.9965	0.070066	0.000047	54.6728	175.5133
	Fe	1.9407	0.298537	0.000708	26.0526	82.7088
120	Co	1.9492	0.082225	0.000090	47.6205	152.0882
	Fe	1.9376	0.342168	0.000956	30.3329	91.5087
140	Co	1.9491	0.097277	0.000104	49.3176	154.9531
	Fe	1.9349	0.350755	0.001005	31.6110	92.9399
168	Co	2.0169	0.056827	0.000034	59.0672	186.9598
	Fe	1.9385	0.275537	0.000614	26.2375	83.8221
200	Co	2.1095	0.049495	0.000023	70.4376	213.3041
	Fe	1.9383	0.157658	0.000284	20.6208	63.8449

Table S17. Hydrogen bonding interactions in 1·2H₂O during heating mode @1 K min⁻¹:

HB interactions (Å)	110 K	120 K	140 K	168 K	200 K
N _{NH2} ···O _{H2O}	2.807	2.795	2.784	2.812	2.855
N _{CN} ···O _{H2O}	2.799	2.796	2.785	2.825	2.869

**Figure S4.** Hydrogen bonding interactions between solvent molecules, perchlorate anions and the [Fe₂(μ-CN)Co₂] square grids along the *ab* plane in complex 1·2H₂O. The Hydrogen atoms not involved in Hydrogen bonding have been omitted for clarity.



2.3. Crystal structure determination of 1:

Figure S5. Crystal Structure of **1**. Colour Code: Green: Fe; Pink: Co; Blue: N; Grey: C; Yellow: B, Dark green: Cl, Light green: F. The hydrogen not involved in H-bonding is omitted for clarity.

Table S18. Crystallographic data of **1**:

Identification code	1
Empirical formula	C ₃₆ H ₂₂ BClCoF ₁₀ FeN ₁₅ O ₄
Formula weight	1079.72
Temperature/K	117.0
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	14.768(3)
b/Å	22.615(6)
c/Å	14.318(4)
α/°	90
β/°	109.286(5)
γ/°	90
Volume/Å ³	4513.6(19)
Z	4
ρ _{calc} /cm ³	1.589
R ₁ ^a	0.0707
wR ₂ ^a	0.1738

Table S19. Selected bond lengths of **1** at 117 K:

Atom	Atom	Bond length/Å
Co1	N15	2.126(6)
Co1	N12	2.103(6)
Co1	N2 ¹	2.112(6)
Co1	N13	2.104(6)
Co1	N9	2.114(6)
Co1	N10	2.127(6)
Fe1	N6	1.968(6)
Fe1	N8	1.976(6)
Fe1	N3	1.965(6)
Fe1	C2	1.900(8)
Fe1	C1	1.929(8)
Fe1	C12	1.896(8)

Table S20. Selected bond angles of **1** at 117 K:

Atoms	Angles/°
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N9	Co1	N2 ¹	85.5(2)
C12	Fe1	C2	90.6(3)

Table S21. Octahedral Shape Analysis of **1** at 117 K:

Octahedral Shape Analysis Value	
Metal centre	117 K
Co	1.137
Fe	0.093

Table S22. Octahedral distortion parameters for **1** at 117 K:

Metal centre	<D> (Å)	Z (Å)	Δ	Σ (°)	Θ (°)
Co	2.1142	0.048023	0.000019	70.9624	211.9373
Fe	1.9388	0.182791	0.000277	19.5784	61.4659

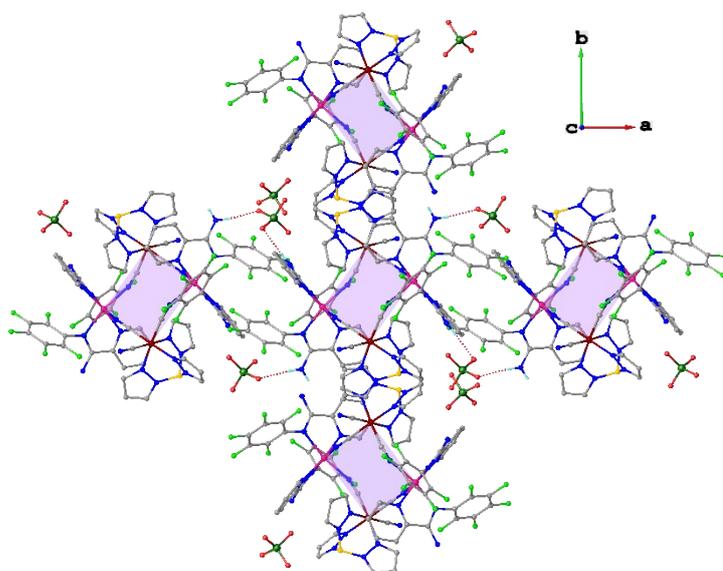


Figure S6. Hydrogen bonding interactions between solvent molecules, perchlorate anions and the $[\text{Fe}_2(\mu\text{-CN})\text{Co}_2]$ square grids along the ab plane in complex **1**. The Hydrogen atoms not involved in Hydrogen bonding have been omitted for clarity.

2.4. Structure overlay:

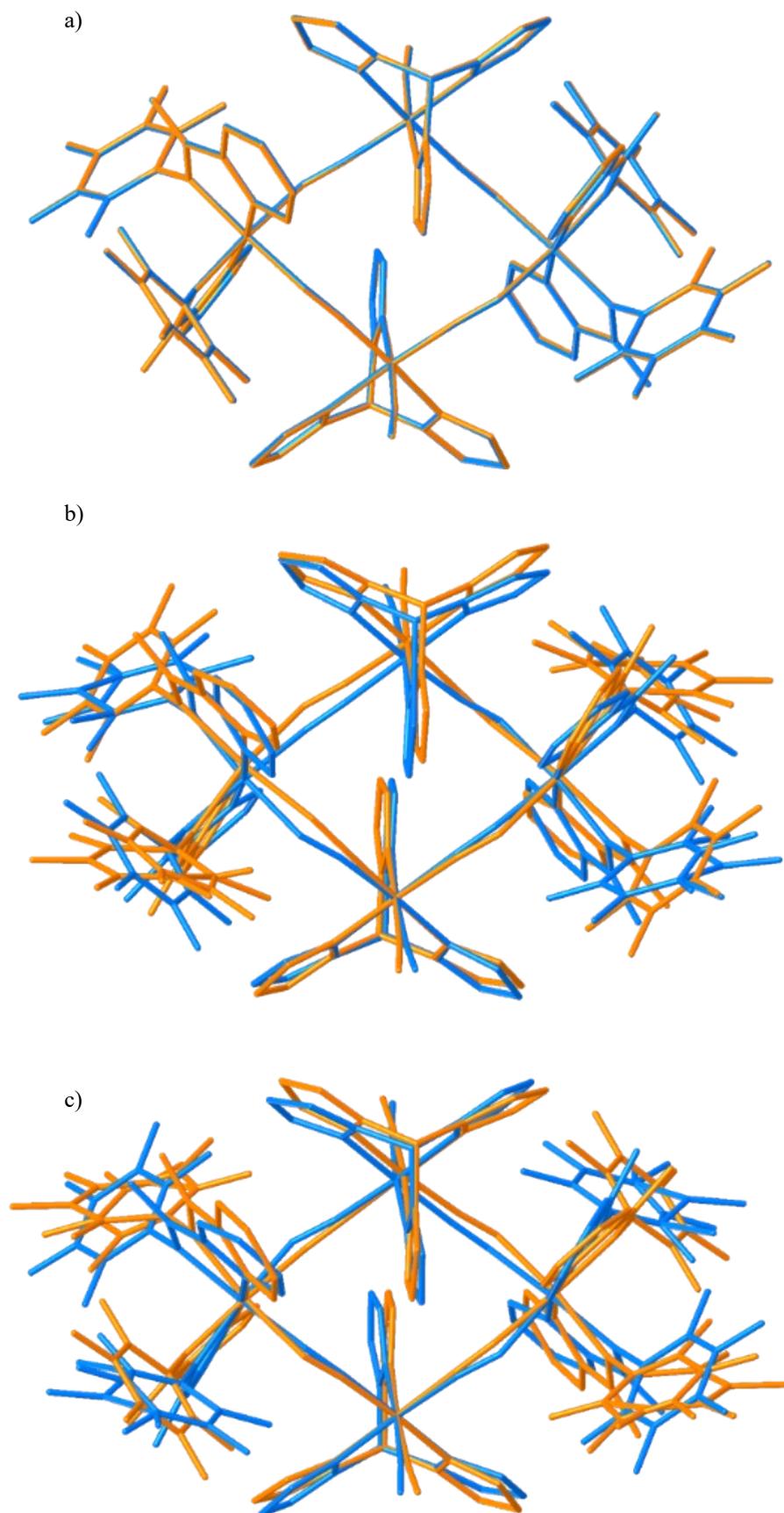


Figure S7. Overlay diagram of a) $1 \cdot 4\text{MeOH} \cdot 2\text{H}_2\text{O}$ (blue: 100 K, orange: 200 K) and b) $1 \cdot 2\text{H}_2\text{O}$ (blue: 140 K, orange: 200 K) and c) $1 \cdot 2\text{H}_2\text{O}$ (blue: 140 K, orange: 110 K). The Hydrogen atoms are omitted for clarity.

2.5. Thermogravimetric analysis:

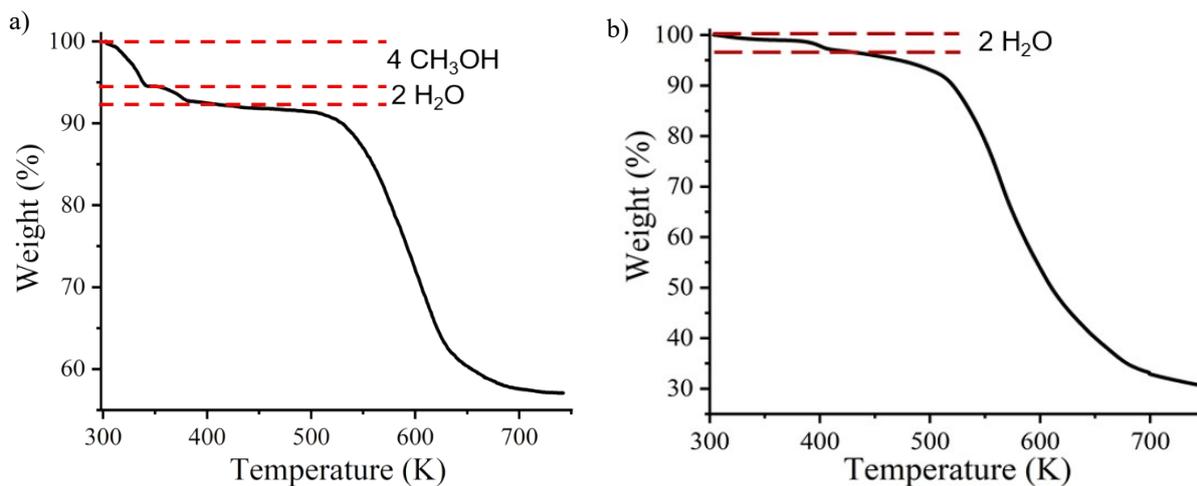


Figure S8. Thermogravimetric analysis of a) $1 \cdot 4\text{MeOH} \cdot 2\text{H}_2\text{O}$, b) $1 \cdot 2\text{H}_2\text{O}$ and c) **1** representing loss of solvent molecules.

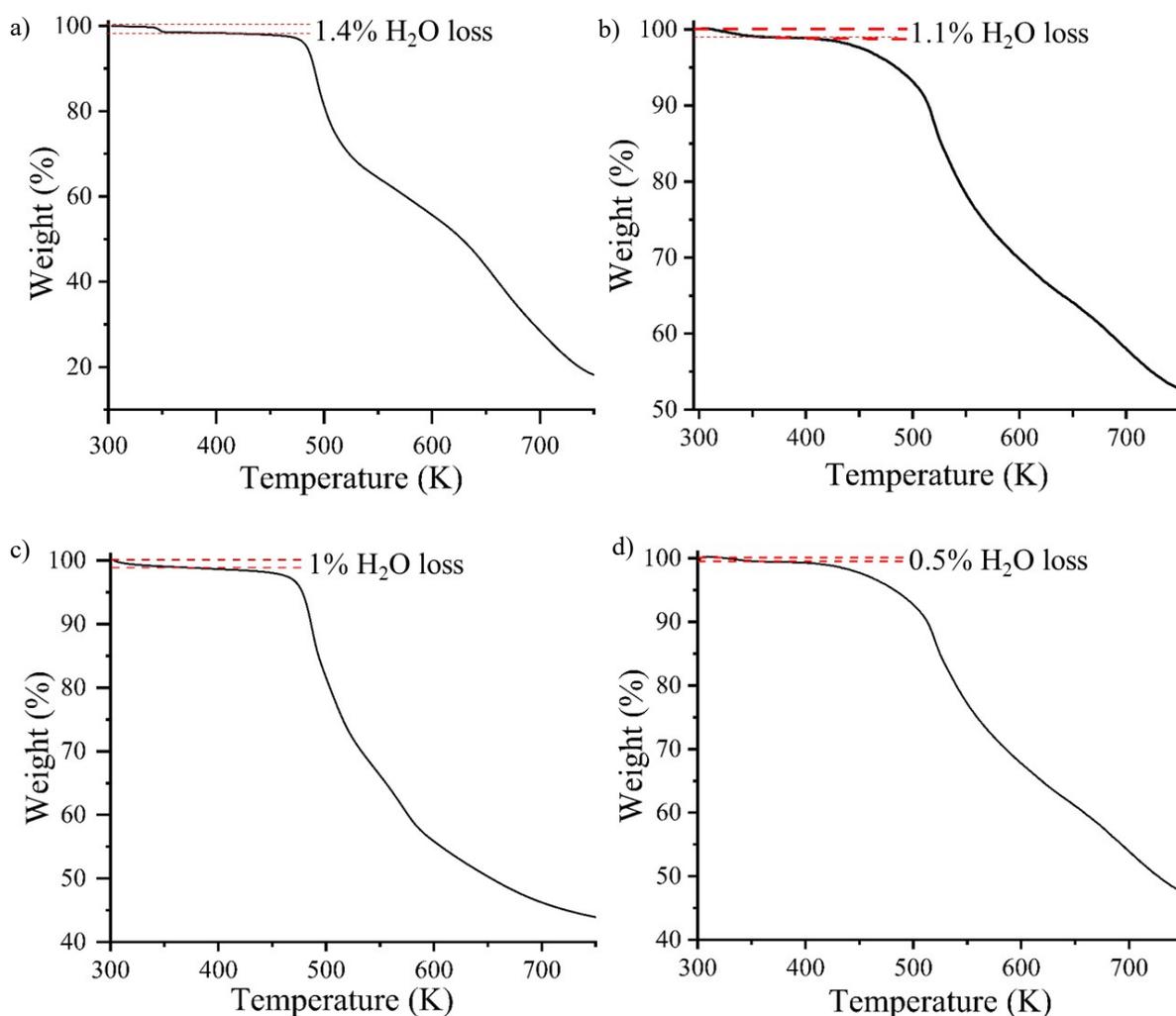


Figure S9. Thermogravimetric analysis of $1 \cdot 2\text{H}_2\text{O}$ after a) 2 days, b) 1 week, c) 2 weeks and d) 4 weeks.

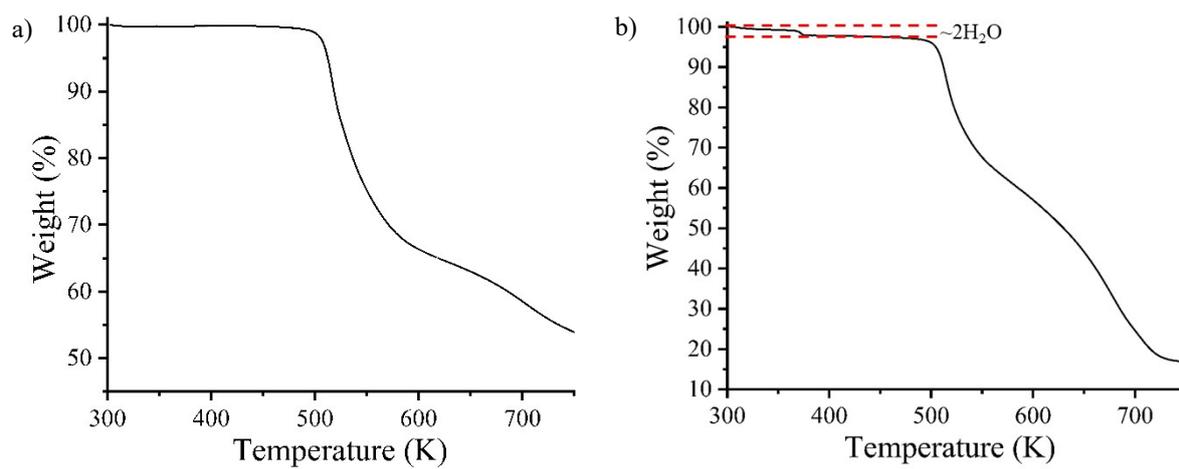


Figure S10. Thermogravimetric analysis of **1** (a) and resolvated complex (b).

2.6. Infrared spectroscopy study:

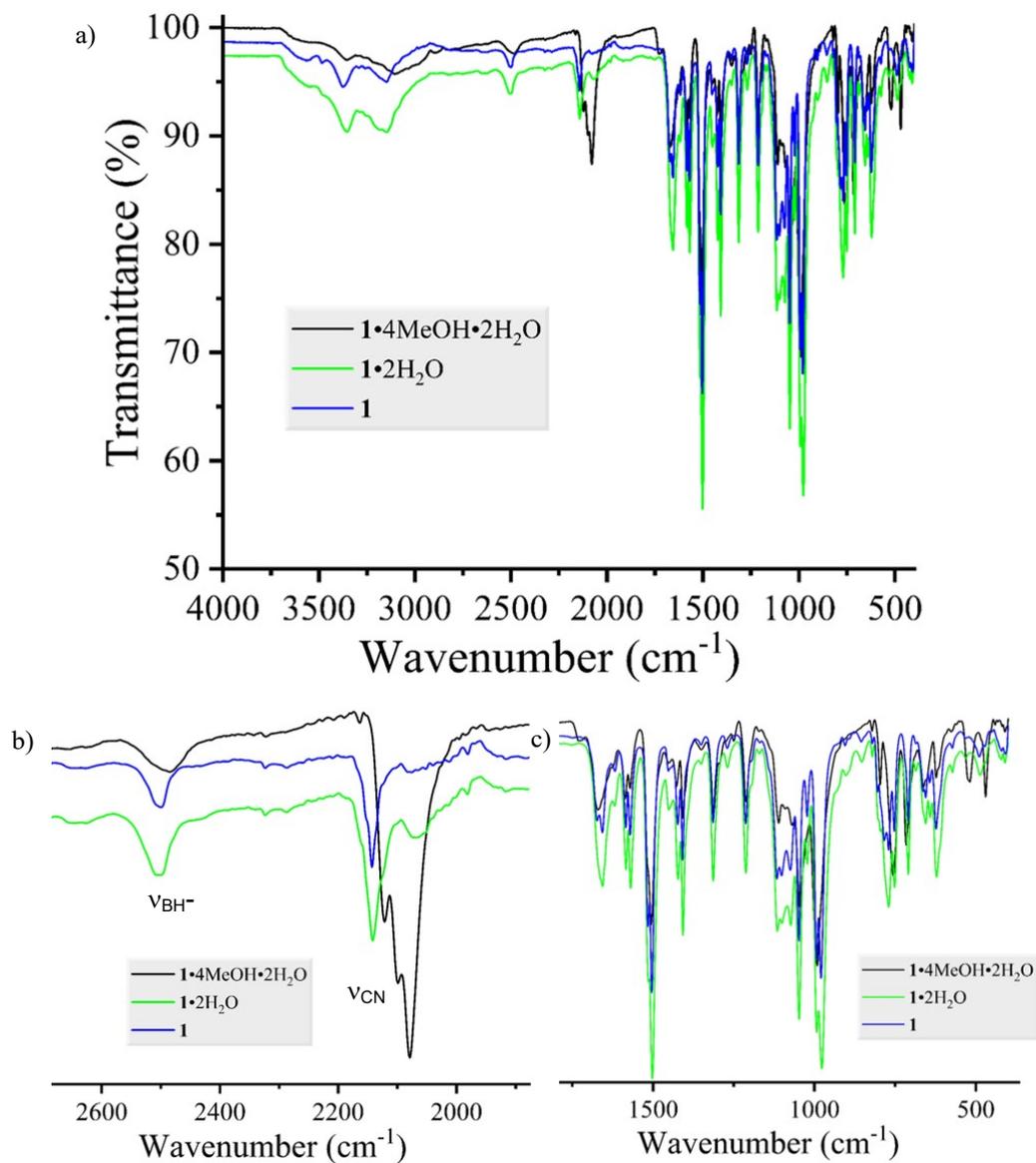


Figure S11. a) Infrared spectroscopy of $1 \cdot 4\text{MeOH} \cdot 2\text{H}_2\text{O}$, $1 \cdot 2\text{H}_2\text{O}$ and **1**. Enlarged view of b) BH^- and CN frequency region and c) 1750 – 400 cm^{-1} .

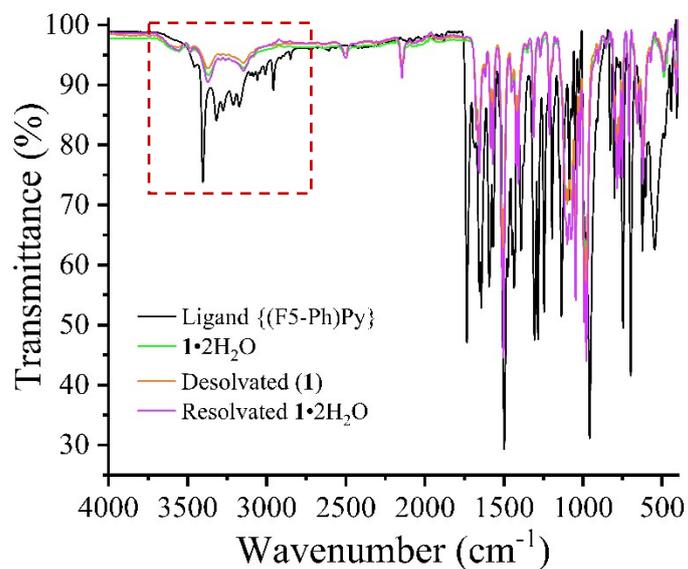


Figure S12. Infrared spectroscopy of ligand, $1 \cdot 2\text{H}_2\text{O}$, desolvated and the resolvated complex.

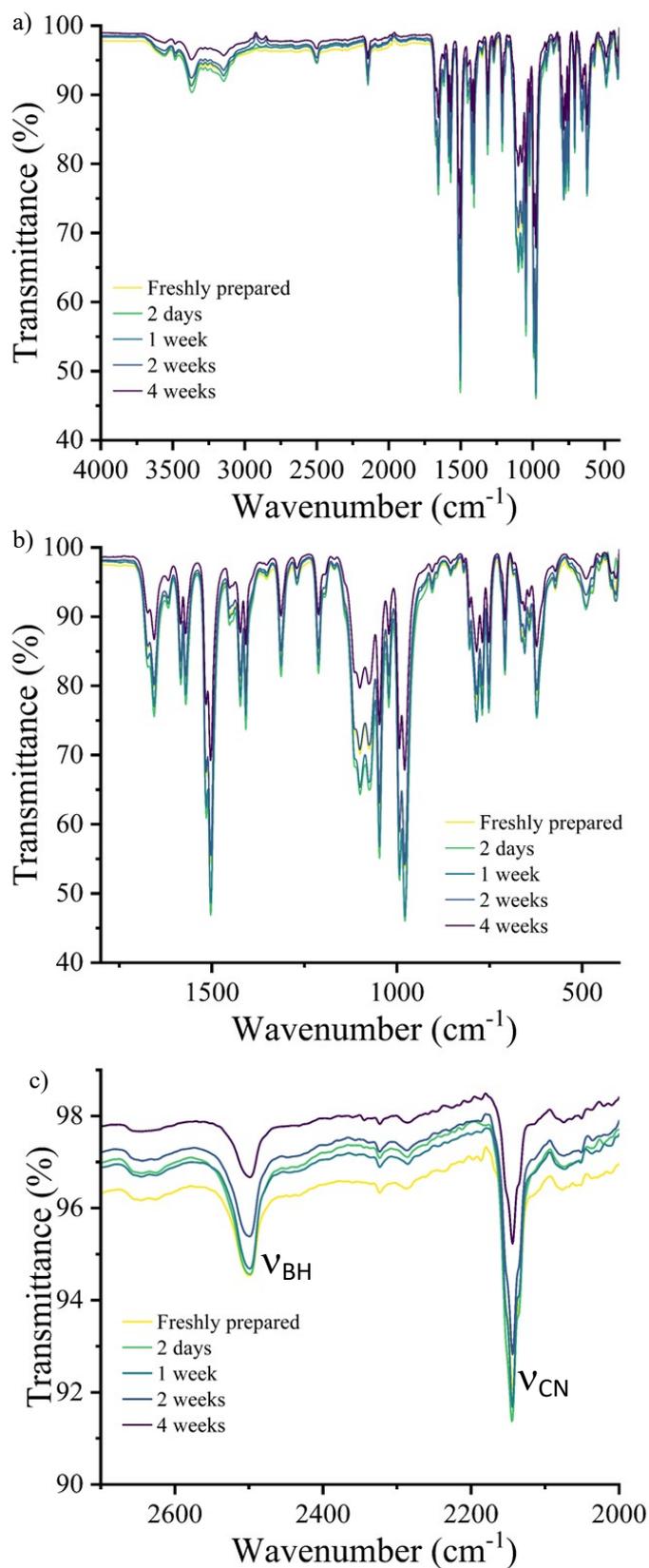


Figure S13. Infrared spectroscopy of $1 \cdot 2\text{H}_2\text{O}$ with ageing a) complete spectra from 4000-400 cm^{-1} , b) fingerprint region (1800-400 cm^{-1}), and c) ν_{BH} and ν_{CN} stretching frequencies.

2.7. Magnetic study:

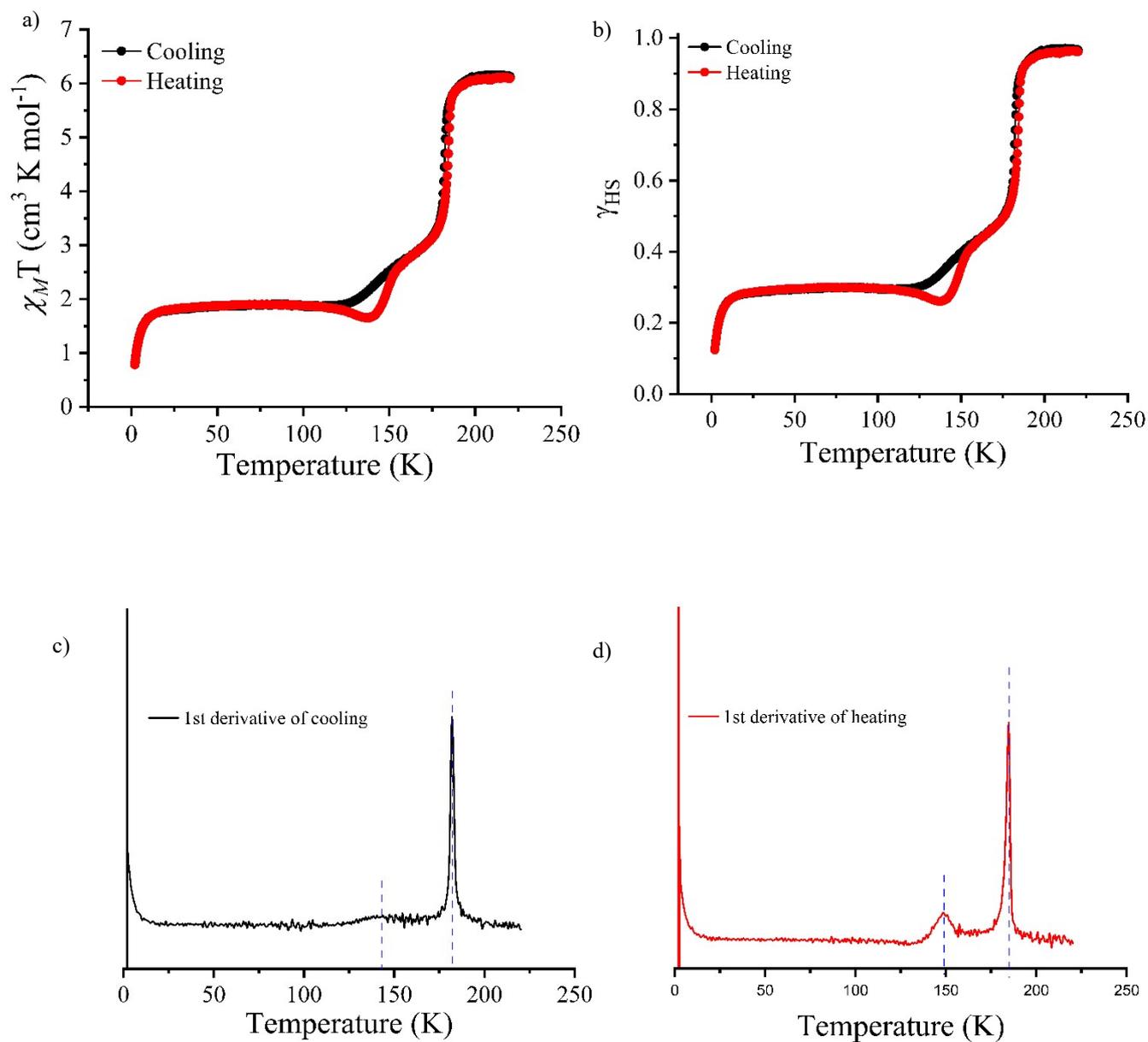


Figure S14. a) $\chi_M T$ vs. T (black), b) γ_{HS} vs. T and c) and d) are the derivative plots during cooling and heating, respectively, for complex $1 \cdot 2H_2O$ at 5 K min^{-1} with applied DC field of 1000 Oe. The separate derivative plot for the complex during the cooling and heating cycle (b and c, respectively).

The HS fraction (γ_{HS}) with temperature is calculated from the equation:

$$\gamma_{HS} = \frac{(\chi_M T)_m - (\chi_M T)_{LS}}{(\chi_M T)_{HS} - (\chi_M T)_{LS}} \dots (1)$$

Here, $(\chi_M T)_m$ corresponds to the $\chi_M T$ value at any measured temperature and $(\chi_M T)_{HS}$ and $(\chi_M T)_{LS}$ represent the $\chi_M T$ values at absolutely populated HS and low spin species of the molecule, respectively.⁵

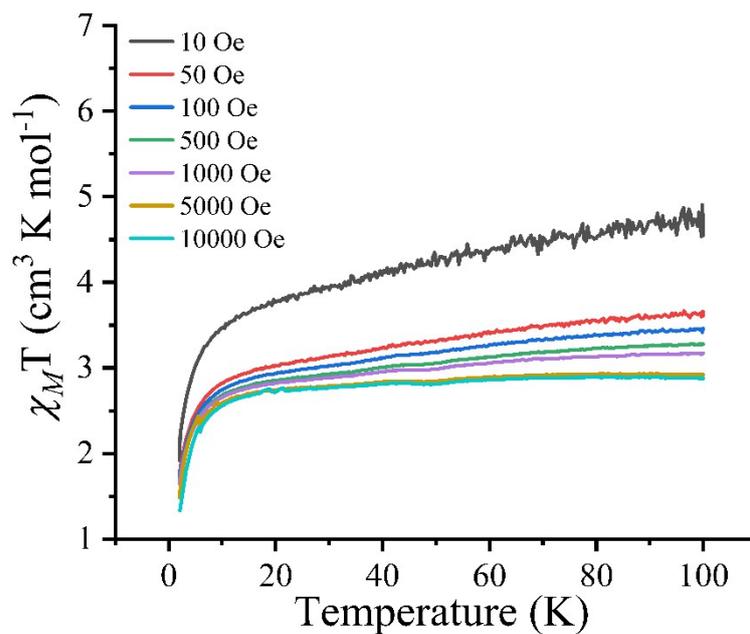


Figure S15. $\chi_M T$ vs. T plots for complex **1**·2H₂O at 5 K min⁻¹ under different applied magnetic field from 10 Oe to 10000 Oe from 2-100 K.

The variation in $\chi_M T$ values observed at 100 K between the two samples in Figures S14 and S15 may be due to multiple measurements performed using the same sample, leading to minor changes in the solvent content over time.

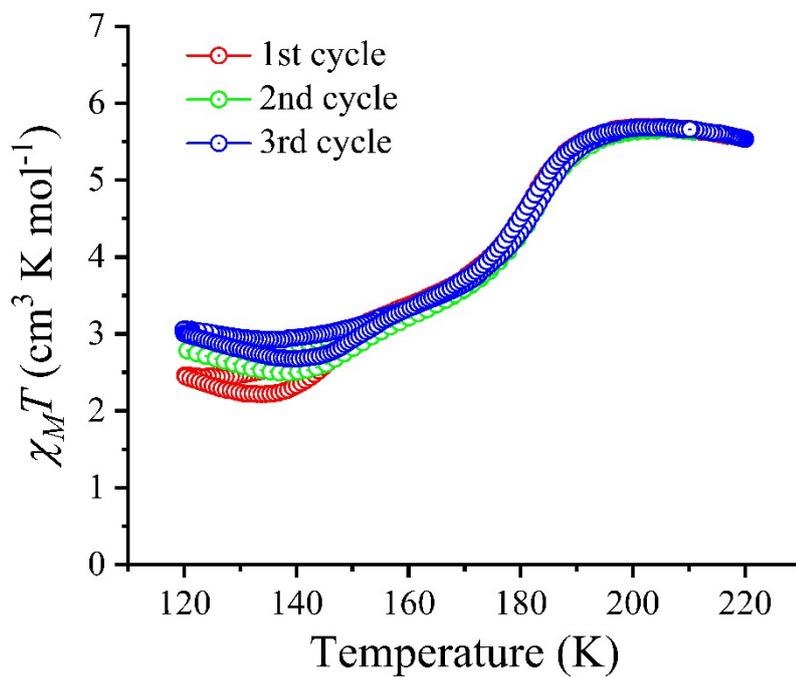


Figure S16. $\chi_M T$ vs. T plot at a scan rate of 5 K min⁻¹ for complex **1**·2H₂O with three consecutive cycles upon resolution.

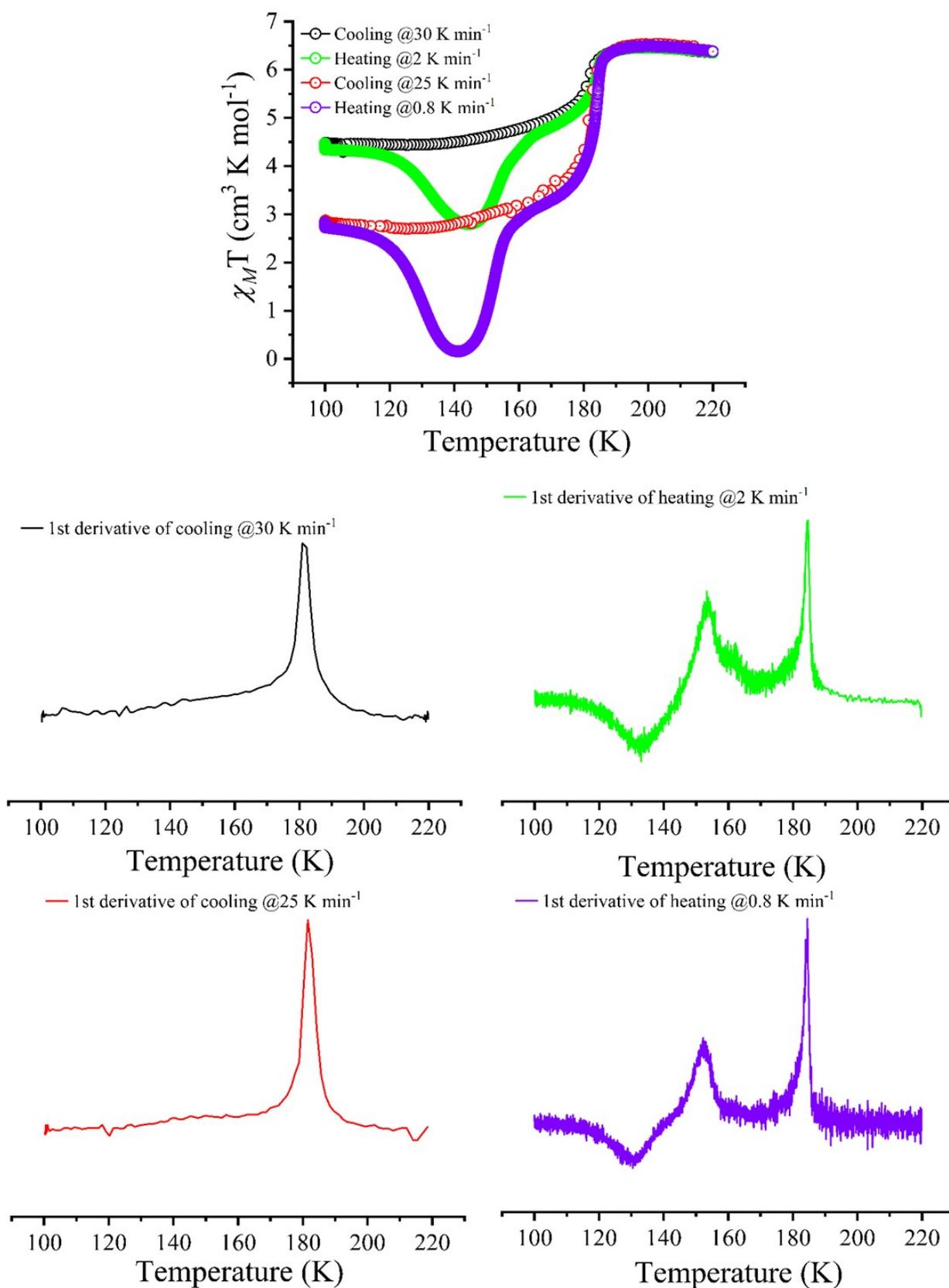


Figure S17. $\chi_M T$ vs. T plots for complex $1 \cdot 2\text{H}_2\text{O}$ upon thermal quenching with a scan rate of 25 K min^{-1} (black) and 30 K min^{-1} (red) via TIESST phenomenon. Heating was measured at a scan rate of 0.8 K min^{-1} (black) and 2 K min^{-1} (red). The 1st derivative plots during cooling and heating mode is shown in their representative colours with single-step and two-step transitions, respectively.

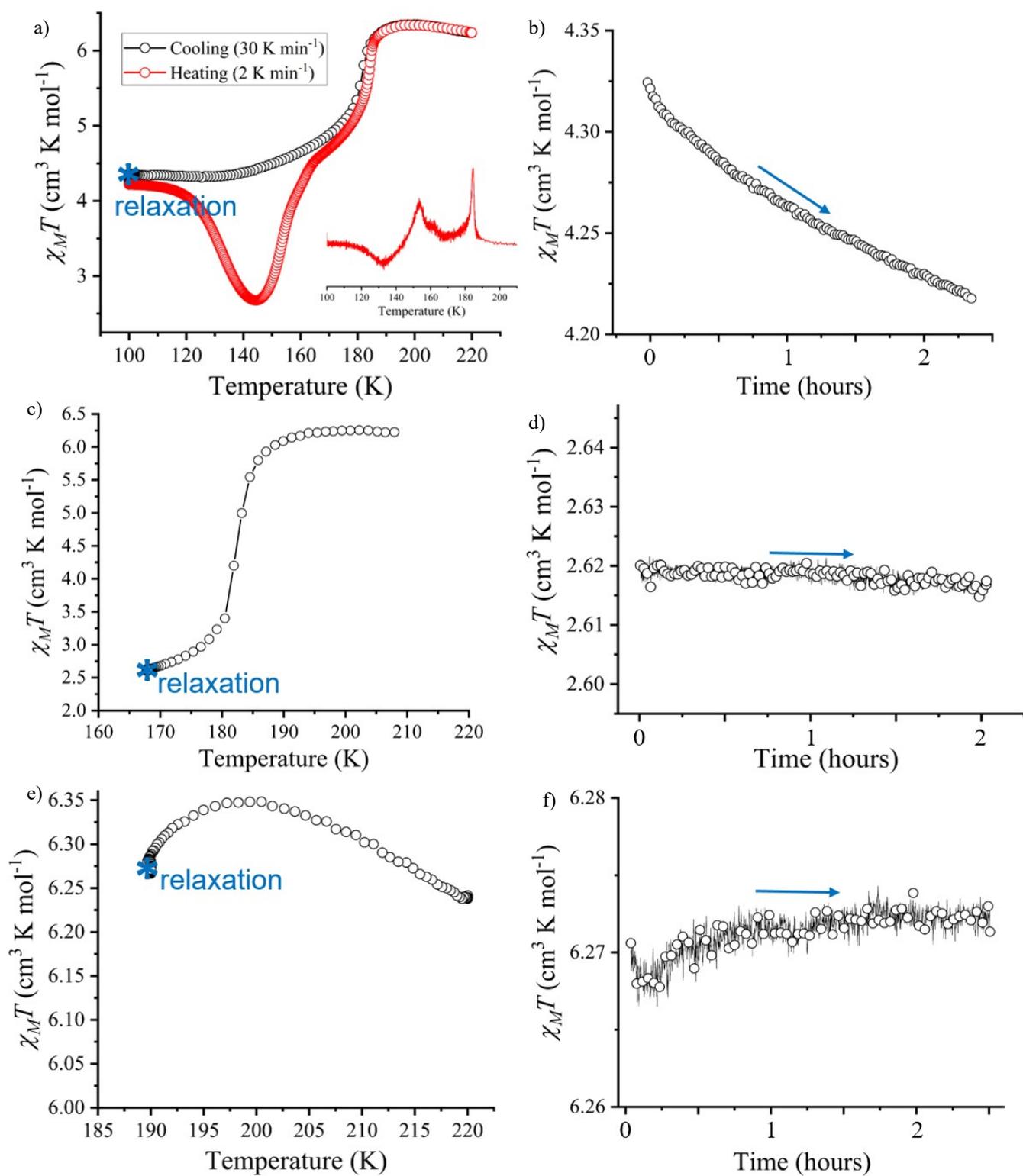


Figure S18. $\chi_M T$ vs. T plots for complex $1 \cdot 2H_2O$ upon thermal quenching with a scan rate of 30 K min⁻¹ upto a) 100 K, c) 168 K and e) 190 K followed by relaxation for about 2 hours at constant temperatures. b), d) and f) $\chi_M T$ vs. time plots at 100 K, 168 K and 190 K, respectively. Inset of a) shows the 1st derivative of heating cycle showing not so prominent three step-transition.

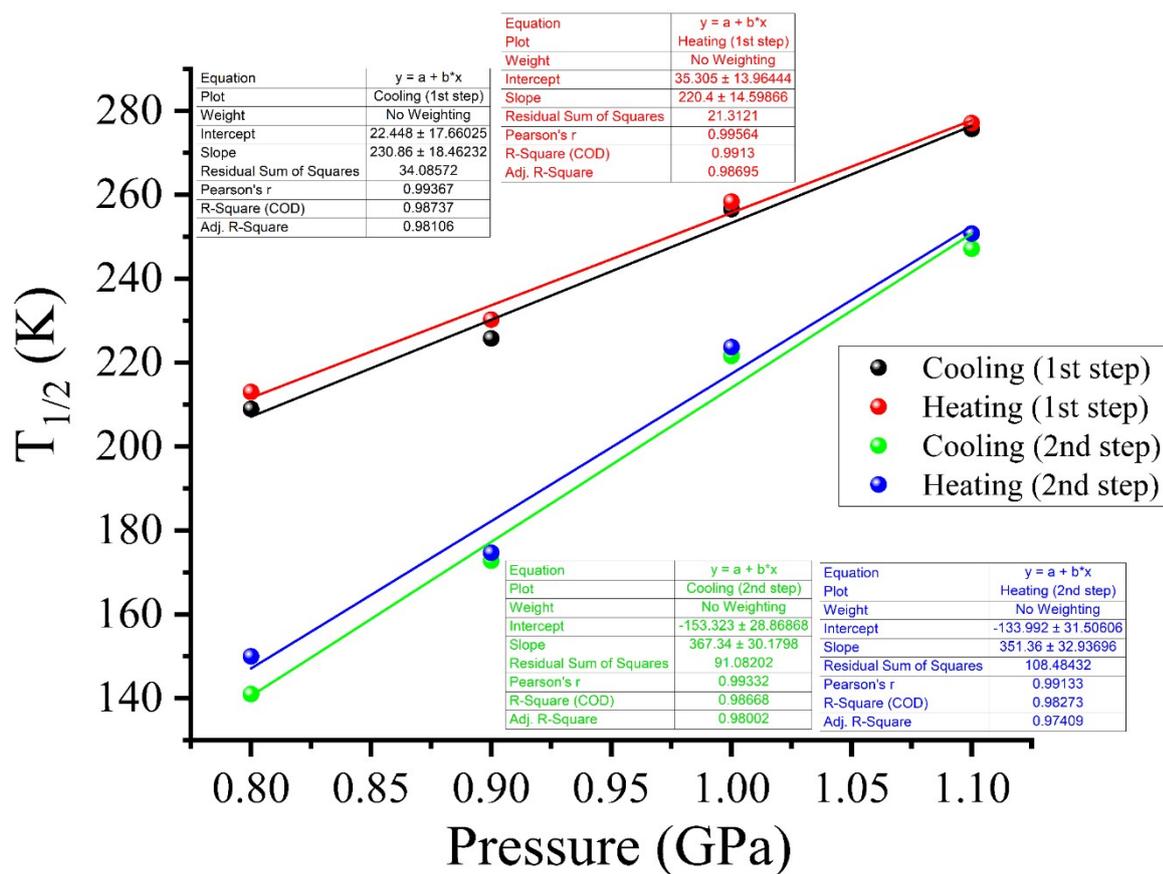


Figure S19. $T_{1/2}$ vs. Pressure plots for complex 1-2H₂O showing linear relation above 0.8 GPa of threshold pressure, following Clayperon law.

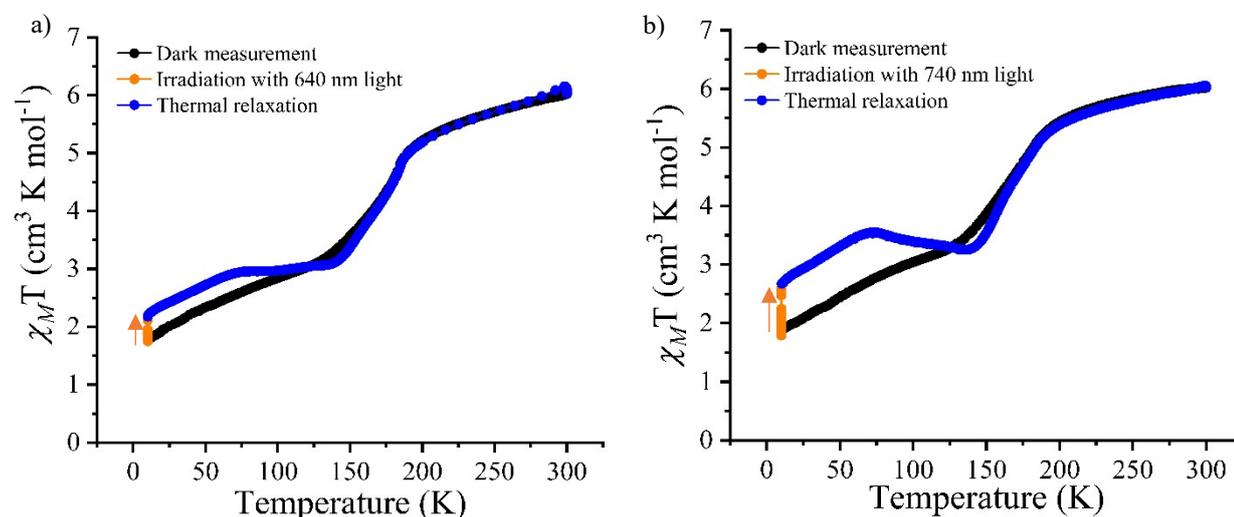


Figure S20. $\chi_M T$ vs. Temperature plots for complex 1-2H₂O with irradiation with a) 640 nm and b) 740 nm of light (orange). The cooling rate is 5 K min⁻¹ (black) and after irradiation, the heating is at 2 K min⁻¹ (blue).

References

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