Supporting Information

Hydration-Dependent Anomalous Thermal Expansion Behaviour in a Coordination Polymer

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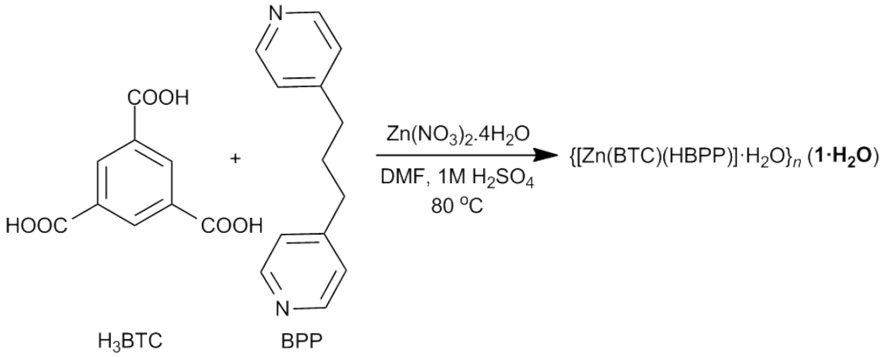
Synthesis

All chemicals and solvent used in these experiments were purchased from Aldrich and used without any further purification.

Synthesis of {[Zn(BTC)(HBPP)]·H_2O}n (1•H_2O)

1,3,5-Benzenetricarboxylic acid (20 mg, 0.095 mmol) and 1,3-bis(4-pyridyl)propane (19 mg, 0.095 mmol) were dissolved in 4.8 mL of DMF whereas $Zn(NO_3)_2$•$4H_2O$ (29 mg, 0.095 mmol) was dissolved in 3.6 mL of ***water*** and acidified with H_2SO_4 (1M, 0.2 mL). Both the solutions were heated and the hot clear solutions were combined in a sealed glass vial. The solution was heated at 80 °C for 24 hours followed by cooling to room temperature. The solution was then kept at -10 °C and after two weeks phase-pure single crystals **1·H_2O** were obtained.



Scheme S1. Synthetic scheme for **1·H_2O**.

Calculation of the coefficients of linear thermal expansion

The unit cell parameters of single crystals of 1.H_2O and 1 were measured at 20 K and 30 K intervals respectively. The results of the measurements are summarised in Tables S1-S3. These values were used to calculate the linear thermal expansion coefficient, α, for each of the axes a, b and c using the following equation:

$\propto=\Delta L/(L\_0\ \Delta T)$

ΔL is the difference in length of the crystallographic axis, L0 is the initial axis length at the initial temperature, T0, and ΔT is the change in temperature. The volumetric expansion coefficient, αV, can be calculated using a modified form of the above equation, i.e. by substituting ΔV for ΔL and V0 for L0. The standard deviations for thermal expansion coefficients are calculated using the "propagation of measurement uncertainty" method.[1] The crystal mosaicity remains approximately the same for the different unit cell determinations.

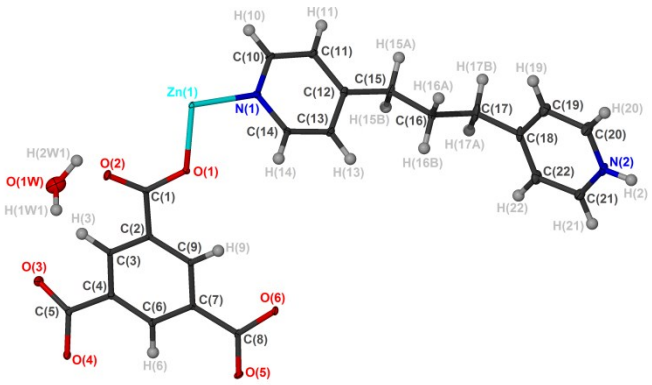


Figure S1. View of Assymmetric Unit in **1·H$_2$O**.

Single Crystal X-ray Diffraction (SCD)

Experimental

Single crystal X-ray diffraction data were collected on a Bruker APEX-II Quasar CCD area-detector diffractometer equipped with an Oxford Cryosystems Cryostream 700Plus cryostat. A multilayer monochromator with $Mo_{K\alpha}$ radiation (λ = 0.71073 Å) from an Incoatec $I_{\mu S}$ microsource was used.

Data reduction was carried out by means of standard procedures using the Bruker software package SAINT[2] and absorption corrections and the correction of other systematic errors were performed using SADABS.[3] The structures were solved by direct methods using SHELXS-97 and refined using SHELXL-97.[4] X-Seed[5] was used as the graphical interface for the SHELX program suite. Hydrogen atoms were placed in calculated positions using riding models.

Table S1. Crystallographic details for 1·H$_2$O

Identification code	**260K**	**240K**	**220K**	**200K**	**180K**
Empirical formula	$C_{22}H_{20}N_2O_7Zn$	$C_{22}H_{20}N_2O_7Zn$	$C_{22}H_{20}N_2O_7Zn$	$C_{22}H_{20}N_2O_7Zn$	$C_{22}H_{20}N_2O_7Zn$
Formula weight	489.77	489.77	489.77	489.77	489.77
Temperature/K	260(2)	240(2)	220(2)	200(2)	180(2)
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*P*na2$_1$	*P*na2$_1$	*P*na2$_1$	*P*na2$_1$	*P*na2$_1$
a/Å	19.1062(9)	19.1136(9)	19.1176(9)	19.1195(9)	19.1196(10)
b/Å	7.8702(4)	7.8642(4)	7.8572(4)	7.8491(4)	7.8379(4)
c/Å	13.7665(7)	13.7696(6)	13.7712(7)	13.7716(7)	13.7729(7)
α/°	90.00	90.00	90.00	90.00	90.00
β/°	90.00	90.00	90.00	90.00	90.00
γ/°	90.00	90.00	90.00	90.00	90.00
Volume/Å^3	2070.06(18)	2069.75(17)	2068.58(18)	2066.72(18)	2063.97(18)
Z	4	4	4	4	4
ρ_{calc}g/cm^3	1.572	1.572	1.573	1.574	1.576
μ/mm^{-1}	1.235	1.235	1.236	1.237	1.239
F(000)	1008	1008	1008	1008	1008
Crystal size/mm^3	0.449 × 0.331 × 0.194	0.449 × 0.331 × 0.194	0.448 × 0.331 × 0.194	0.447 × 0.331 × 0.194	0.447 × 0.331 × 0.194
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
θ range for data collection/°	2.13 to 25.97	2.13 to 26.00	2.13 to 26.01	2.13 to 26.00	2.13 to 26.01
Index ranges	-23 ≤ h ≤ 23, -9 ≤ k ≤ 5, -16 ≤ l ≤ 16	-23 ≤ h ≤ 23, -9 ≤ k ≤ 5, -16 ≤ l ≤ 16	-23 ≤ h ≤ 23, -9 ≤ k ≤ 5, -17 ≤ l ≤ 16	-23 ≤ h ≤ 23, -9 ≤ k ≤ 5, -16 ≤ l ≤ 16	-23 ≤ h ≤ 23, -9 ≤ k ≤ 5, -17 ≤ l ≤ 16
Reflections collected	10710	10748	10746	10737	10711
Independent reflections	4025 [R_{int} =	4041 [R_{int} =	4043 [R_{int} = 0.0231,	4039 [R_{int} = 0.0231,	4032 [R_{int} =

	0.0236, R_{sigma} = 0.0439]	0.0237, R_{sigma} = 0.0457]	R_{sigma} = 0.0447]	R_{sigma} = 0.0446]	0.0224, R_{sigma} = 0.0442]
Data/restraints/parameters	4025/4/289	4041/4/289	4043/4/289	4039/4/289	4032/4/289
Goodness-of-fit on F^2	1.062	1.074	1.084	1.060	1.092
Final R indexes [I>=2σ (I)]	R_1 = 0.0284, wR_2 = 0.0751	R_1 = 0.0274, wR_2 = 0.0732	R_1 = 0.0269, wR_2 = 0.0692	R_1 = 0.0258, wR_2 = 0.0665	R_1 = 0.0255, wR_2 = 0.0651
Final R indexes [all data]	R_1 = 0.0314, wR_2 = 0.0770	R_1 = 0.0297, wR_2 = 0.0746	R_1 = 0.0293, wR_2 = 0.0703	R_1 = 0.0278, wR_2 = 0.0675	R_1 = 0.0278, wR_2 = 0.0663
Largest diff. peak/hole / e Å^{-3}	0.286/-0.508	0.296/-0.475	0.272/-0.484	0.248/-0.523	0.263/-0.540
Mosaicity	0.36	0.35	0.36	0.36	0.36

Identification code	**160K**	**140K**	**120K**	**100K**	**260K-R**
Empirical formula	$C_{22}H_{20}N_2O_7Zn$	$C_{22}H_{20}N_2O_7Zn$	$C_{22}H_{20}N_2O_7Zn$	$C_{22}H_{20}N_2O_7Zn$	$C_{22}H_{20}N_2O_7Zn$
Formula weight	489.77	489.77	489.77	489.77	489.77
Temperature/K	160(2)	140(2)	120(2)	100(2)	260R(2)
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*P*na2$_1$	*P*na2$_1$	*P*na2$_1$	*P*na2$_1$	*P*na2$_1$
a/Å	19.1211(10)	19.1203(11)	19.1221(11)	19.1246(11)	19.1073(9)
b/Å	7.8289(4)	7.8191(4)	7.8119(5)	7.8040(5)	7.8706(4)
c/Å	13.7769(8)	13.7785(8)	13.7812(8)	13.7839(8)	13.7668(6)
α/°	90.00	90.00	90.00	90.00	90.00
β/°	90.00	90.00	90.00	90.00	90.00
γ/°	90.00	90.00	90.00	90.00	90.00
Volume/Å^3	2062.36(19)	2059.9(2)	2058.6(2)	2057.2(2)	2070.33(17)
Z	4	4	4	4	4
ρ_{calc}g/cm^3	1.577	1.579	1.580	1.581	1.571
μ/mm^{-1}	1.240	1.241	1.242	1.243	1.235
F(000)	1008	1008	1008	1008	1008
Crystal size/mm^3	0.446 × 0.331 × 0.194	0.446 × 0.331 × 0.194	0.445 × 0.331 × 0.194	0.445 × 0.331 × 0.194	0.449 × 0.331 × 0.194
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
θ range for data collection/°	2.13 to 26.00	2.13 to 25.99	2.13 to 26.02	2.13 to 25.97	2.13 to 25.99
Index ranges	-23 ≤ h ≤ 23, -9 ≤ k ≤ 5, -16 ≤ l ≤ 16	-23 ≤ h ≤ 23, -9 ≤ k ≤ 5, -16 ≤ l ≤ 16	-23 ≤ h ≤ 23, -9 ≤ k ≤ 4, -17 ≤ l ≤ 16	-23 ≤ h ≤ 23, -9 ≤ k ≤ 4, -16 ≤ l ≤ 16	-23 ≤ h ≤ 23, -9 ≤ k ≤ 5, -16 ≤ l ≤ 16
Reflections collected	10672	10643	10650	10608	10740
Independent reflections	4017 [R_{int} = 0.0224, R_{sigma} = 0.0429]	4005 [R_{int} = 0.0225, R_{sigma} = 0.0443]	4011 [R_{int} = 0.0223, R_{sigma} = 0.0433]	3994 [R_{int} = 0.0220, R_{sigma} = 0.0433]	4032 [R_{int} = 0.0237, R_{sigma} = 0.0447]
Data/restraints/parameters	4017/4/289	4005/4/289	4011/4/289	3994/4/289	4032/4/289
Goodness-of-fit on F^2	1.099	1.104	1.092	1.095	1.067
Final R indexes [I>=2σ (I)]	R_1 = 0.0258, wR_2 = 0.0669	R_1 = 0.0258, wR_2 = 0.0669	R_1 = 0.0258, wR_2 = 0.0659	R_1 = 0.0257, wR_2 = 0.0674	R_1 = 0.0288, wR_2 = 0.0754
Final R indexes [all data]	R_1 = 0.0280, wR_2 = 0.0680	R_1 = 0.0275, wR_2 = 0.0678	R_1 = 0.0276, wR_2 = 0.0669	R_1 = 0.0275, wR_2 = 0.0684	R_1 = 0.0317, wR_2 = 0.0771
Largest diff. peak/hole / e Å^{-3}	0.392/-0.514	0.406/-0.533	0.446/-0.538	0.440/-0.508	0.321/-0.504
Mosaicity	0.36	0.36	0.36	0.36	0.35

Table S2. **Unit cell axes and cell volume at variable temperatures for 1·H_2O**.

***T* (K)**	***a* (Å)**	**St. dev.***	***b* (Å)**	**St. dev.***	***c* (Å)**	**St. dev. ***	**V(Å^3)**	**St. dev.***	**Crystal mosaicity**
260	19.1062	0.0009	7.8702	0.0004	13.7665	0.0007	2070.06	0.18	0.36
240	19.1136	0.0009	7.8642	0.0004	13.7696	0.0006	2069.75	0.17	0.35
220	19.1176	0.0009	7.8572	0.0004	13.7712	0.0007	2068.58	0.18	0.36
200	19.1195	0.0009	7.8491	0.0004	13.7716	0.0007	2066.72	0.18	0.36
180	19.1196	0.0010	7.8379	0.0004	13.7729	0.0007	2063.97	0.18	0.36
160	19.1211	0.0010	7.8289	0.0004	13.7769	0.0008	2062.36	0.19	0.36
140	19.1203	0.0011	7.8191	0.0004	13.7785	0.0008	2059.9	0.2	0.36
120	19.1221	0.0011	7.8119	0.0005	13.7812	0.0008	2058.6	0.2	0.36
100	19.1246	0.0011	7.8040	0.0005	13.7839	0.0008	2057.2	0.2	0.36
260-R	19.1073	0.0009	7.8706	0.0004	13.7668	0.0006	2070.33	0.17	0.35

*Standard deviation calculated from unit cell refinement using the Apex II software suite.

Table S3. Crystallographic details for 1

Identification code	**310K**	**280K**	**250K**	**220K**	**190K**
Empirical formula	$C_{22}H_{18}N_2O_6Zn$	$C_{22}H_{18}N_2O_6Zn$	$C_{22}H_{18}N_2O_6Zn$	$C_{22}H_{18}N_2O_6Zn$	$C_{22}H_{18}N_2O_6Zn$
Formula weight	471.75	471.75	471.75	471.75	471.75
Temperature/K	310(2)	280(2)	250(2)	220(2)	190(2)
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$Pna2_1$	$Pna2_1$	$Pna2_1$	$Pna2_1$	$Pna2_1$
a/Å	18.972(2)	18.9725(19)	18.9745(19)	18.983(2)	18.977(2)
b/Å	7.8309(9)	7.8178(8)	7.8080(8)	7.8009(9)	7.7881(9)
c/Å	13.6741(15)	13.6767(14)	13.6816(14)	13.6902(16)	13.6890(15)
α/°	90.00	90.00	90.00	90.00	90.00
β/°	90.00	90.00	90.00	90.00	90.00
γ/°	90.00	90.00	90.00	90.00	90.00
Volume/Å^3	2031.6(4)	2028.6(4)	2027.0(4)	2027.3(4)	2023.2(4)
Z	4	4	4	4	4
ρ_{calc}g/cm^3	1.542	1.545	1.546	1.546	1.549
μ/mm^{-1}	1.252	1.254	1.255	1.255	1.257
F(000)	968	968	968	968	968
Crystal size/mm^3	0.553× 0.208 × 0.186	0.552× 0.208 × 0.186	0.552× 0.208 × 0.186	0.551× 0.208 × 0.186	0.550× 0.208 × 0.186
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
θ range for data collection/°	2.15 to 26.00	2.15 to 25.97	2.15 to 25.97	2.15 to 25.97	2.15 to 25.97
Index ranges	-23 ≤ h ≤ 18, -9 ≤ k ≤ 7, -16 ≤ l ≤ 16	-23 ≤ h ≤ 18, -9 ≤ k ≤ 7, -16 ≤ l ≤ 16	-18 ≤ h ≤ 23, -9 ≤ k ≤ 7, -16 ≤ l ≤ 16	-18 ≤ h ≤ 23, -9 ≤ k ≤ 7, -16 ≤ l ≤ 16	-18 ≤ h ≤ 23, -9 ≤ k ≤ 7, -16 ≤ l ≤ 16
Reflections collected	10474	10535	10515	10089	10419
Independent reflections	3940 [R_{int} = 0.0373, R_{sigma} = 0.0559]	3932 [R_{int} = 0.0357, R_{sigma} = 0.0542]	3927 [R_{int} = 0.0362, R_{sigma} = 0.0550]	3916 [R_{int} = 0.0360, R_{sigma} = 0.0546]	3911 [R_{int} = 0.0343, R_{sigma} = 0.0531]
Data/restraints/parameters	3940/1/280	3932/1/280	3927/1/280	3916/1/280	3911/1/280
Goodness-of-fit on F^2	1.030	1.044	1.045	1.057	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0415, wR_2 = 0.0962	R_1 = 0.0396, wR_2 = 0.0930	R_1 = 0.0406, wR_2 = 0.0977	R_1 = 0.0387, wR_2 = 0.0918	R_1 = 0.0370, wR_2 = 0.0897
Final R indexes [all data]	R_1 = 0.0535, wR_2 = 0.1018	R_1 = 0.0509, wR_2 = 0.0979	R_1 = 0.0509, wR_2 = 0.1029	R_1 = 0.0477, wR_2 = 0.0958	R_1 = 0.0446, wR_2 = 0.0935
Largest diff. peak/hole / e Å^{-3}	0.527/-0.306	0.494/-0.290	0.740/-0.275	0.655/-0.323	0.612/-0.285
Mosaicity	0.34	0.34	0.34	0.34	0.34

Identification code	**160K**	**130K**	**100K**	**310K-R**
Empirical formula	$C_{22}H_{18}N_2O_6Zn$	$C_{22}H_{18}N_2O_6Zn$	$C_{22}H_{18}N_2O_6Zn$	$C_{22}H_{18}N_2O_6Zn$
Formula weight	471.75	471.75	471.75	471.75
Temperature/K	160(2)	130(2)	100(2)	310R(2)
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$Pna2_1$	$Pna2_1$	$Pna2_1$	$Pna2_1$
a/Å	18.976(2)	18.9781(18)	18.9732(17)	18.973(2)
b/Å	7.7768(8)	7.7660(8)	7.7530(7)	7.8316(9)
c/Å	13.6920(14)	13.6963(13)	13.6972(12)	13.6758(15)
α/°	90.00	90.00	90.00	90.00
β/°	90.00	90.00	90.00	90.00
γ/°	90.00	90.00	90.00	90.00
Volume/Å^3	2020.6(4)	2018.6(3)	2014.8(3)	2032.1(4)
Z	4	4	4	4
ρ_{calc}g/cm^3	1.551	1.552	1.555	1.542
μ/mm^{-1}	1.259	1.260	1.262	1.252
F(000)	968	968	968	968
Crystal size/mm^3	0.549× 0.208 × 0.186	0.549× 0.208 × 0.186	0.548× 0.208 × 0.186	0.553× 0.208 × 0.186
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
θ range for data collection/°	2.15 to 25.97	2.15 to 25.97	2.15 to 25.96	2.15 to 25.98
Index ranges	-18 ≤ h ≤ 23, -9 ≤ k ≤ 7, -16 ≤ l ≤ 16	-18 ≤ h ≤ 23, -9 ≤ k ≤ 7, -16 ≤ l ≤ 16	-18 ≤ h ≤ 23, -9 ≤ k ≤ 7, -16 ≤ l ≤ 16	-23 ≤ h ≤ 18, -9 ≤ k ≤ 7, -16 ≤ l ≤ 16
Reflections collected	10418	10380	10386	10539
Independent reflections	3908 [R_{int} =	3901 [R_{int} =	3896 [R_{int} =	3946 [R_{int} =

	0.0340, R_{sigma} = 0.0524]	0.0336, R_{sigma} = 0.0524]	0.0326, R_{sigma} = 0.0504]	0.0381, R_{sigma} = 0.0567]
Data/restraints/parameters	3908/1/280	3901/1/280	3896/1/280	3946/1/280
Goodness-of-fit on F^2	1.061	1.060	1.059	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0363, wR_2 = 0.0860	R_1 = 0.0360, wR_2 = 0.0866	R_1 = 0.0354, wR_2 = 0.0854	R_1 = 0.0416, wR_2 = 0.0964
Final R indexes [all data]	R_1 = 0.0434, wR_2 = 0.0893	R_1 = 0.0425, wR_2 = 0.0901	R_1 = 0.0409, wR_2 = 0.0881	R_1 = 0.0547, wR_2 = 0.1023
Largest diff. peak/hole / e $Å^{-3}$	0.743/-0.320	0.709/-0.248	0.669/-0.251	0.585/-0.323
Mosaicity	0.34	0.34	0.34	0.34

Table S4. **Unit cell axes and cell volume at variable temperatures for 1**.

T **(K)**	***a*** **(Å)**	**St. dev.***	***b*** **(Å)**	**St. dev.***	***c*** **(Å)**	**St. dev.***	**V(Å³)**	**St. dev.***	**Crystal mosaicity**
310	18.972	0.002	7.8309	0.0009	13.6741	0.0015	2031.6	0.4	0.34
280	18.9725	0.0019	7.8178	0.0008	13.6767	0.0014	2028.6	0.4	0.34
250	18.9745	0.0019	7.8080	0.0008	13.6816	0.0014	2027.0	0.4	0.34
220	18.983	0.002	7.8009	0.0009	13.6902	0.0016	2027.3	0.4	0.34
190	18.977	0.002	7.7881	0.0009	13.6890	0.0015	2023.2	0.4	0.34
160	18.976	0.002	7.7768	0.0008	13.6920	0.0014	2020.6	0.4	0.34
130	18.9781	0.0018	7.7660	0.0008	13.6963	0.0013	2018.6	0.3	0.34
100	18.9732	0.0017	7.7530	0.0007	13.6972	0.0012	2014.8	0.3	0.34
310-R	18.973	0.002	7.8316	0.0009	13.6758	0.0015	2032.1	0.4	0.34

*Standard deviation calculated from unit cell refinement using the Apex II software suite.

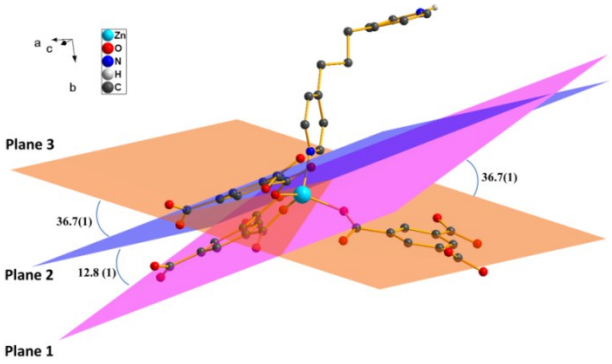


Figure S2. Perspective view of dihedral angles in **1**·H_2O.

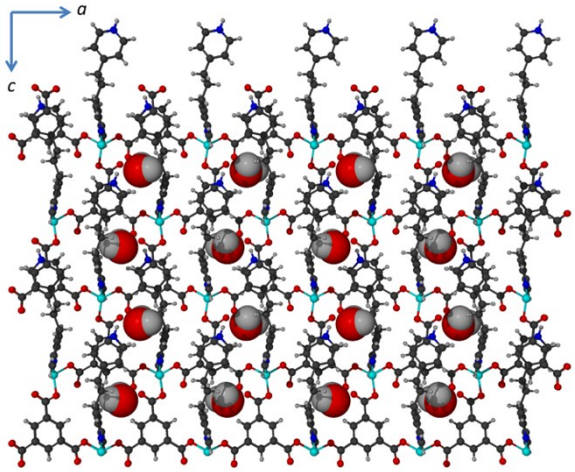


Figure S3. View of overall packing arrangement of **1**·H_2O showing the included water molecules (for clarity the main framework has been shown in the ball-stick model and the water molecules are represented as CPK models).

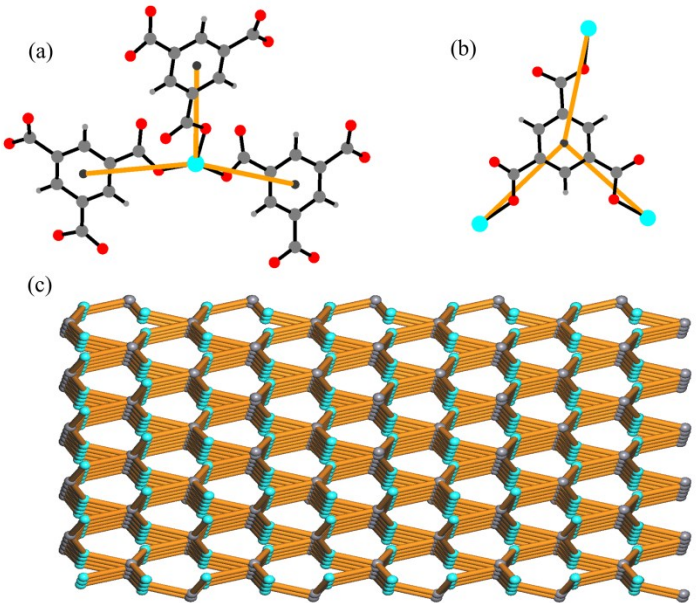


Figure S3. Perspective view of (a) 3-connected Zn node, (b) 3-connected ligand node and (c) (10,3)-d (**utp**) net topology **1**·**H$_2$O**.

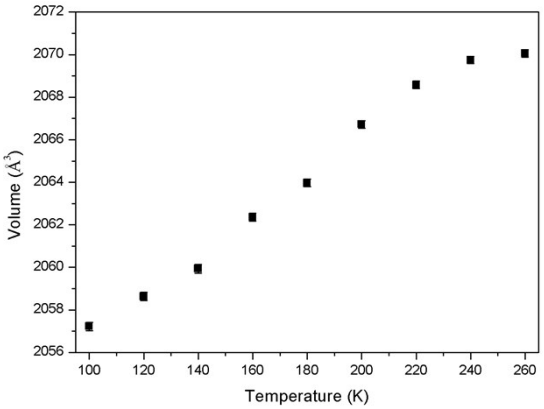


Figure S5. Variation of unit cell volume of **1**·**H$_2$O** (including standard deviations) with temperature.

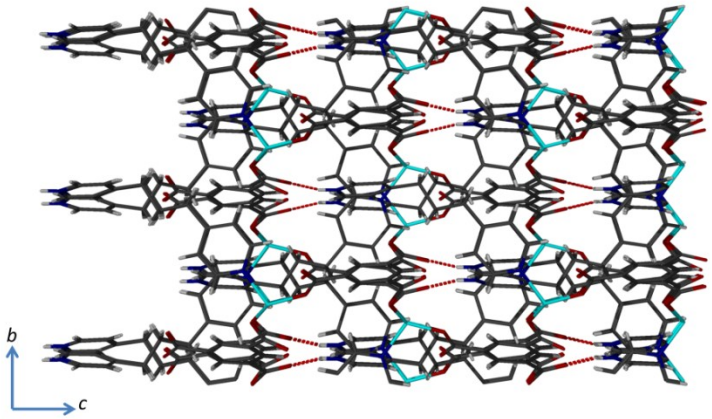


Figure S6. View of overall packing arrangement of **1**·H$_2$O showing the N–H···O hydrogen bonding interactions (water molecules are removed for clarity).

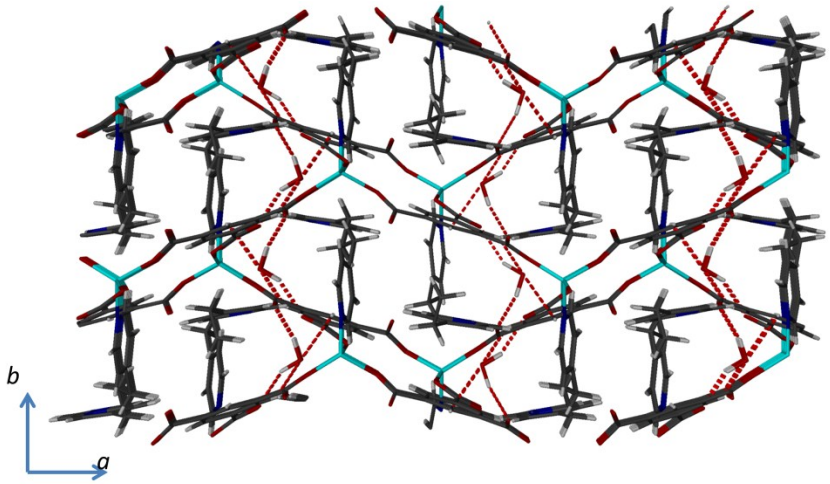


Figure S7. View of overall packing arrangement of **1**·H_2O showing the O–H···O and C–H···O hydrogen bonding interactions.

Table S5. List of selected angles and torsional angles in **1·H_2O** in the temperature range 260 K and 100 K.

T(K)	C15··· C16···C17 (θ_1)	N1··· C12··· C18···N2 (φ_1)
260	111.5(3)	7.4(5)
240	111.6(3)	7.4(5)
220	111.2(2)	7.1(4)
200	111.0(2)	7.6(4)
180	110.9(2)	7.3(4)
160	111.3(2)	7.0(4)
140	110.8(2)	6.7(4)
120	110.9(2)	6.5(4)
100	110.7(2)	6.3(4)

Table S6. List of Screw pitch and diameter of helices in **1·H_2O** in the temperature range 260 K and 100 K.

T(K)	Screw Pitch (Å)	Diameter (Å)
260	7.870(1)	11.239(3)
240	7.864(1)	11.246(3)
220	7.857(1)	11.249(3)
200	7.849(1)	11.250(3)
180	7.838(1)	11.255(3)
160	7.829(1)	11.255(3)
140	7.819(1)	11.256(3)
120	7.812(1)	11.259(3)
100	7.804(1)	11.262(3)

Table S7. List of N–H···O hydrogen bonding interactions in **1·H_2O** in the temperature range 260 K and 100 K.

T(K)	d(N–H)	d(H···O)	d(N···O)	<NHO
260	0.860(3)	1.871(2)	2.711(4)	165.1(2)
240	0.870(3)	1.863(2)	2.712(4)	165.0(2)
220	0.870(3)	1.855(2)	2.705(3)	165.0(2)
200	0.880(2)	1.845(2)	2.703(3)	164.5(2)
180	0.880(2)	1.845(2)	2.703(3)	164.6(2)
160	0.880(2)	1.841(2)	2.699(3)	164.3(2)
140	0.880(3)	1.839(2)	2.697(3)	164.4(2)
120	0.880(2)	1.838(2)	2.695(3)	164.2(2)
100	0.880(2)	1.838(2)	2.695(3)	163.9(2)

Table S8. List of O–H···O hydrogen bonding interactions in **1·H_2O** in the temperature range 260 K and 100 K.

	O1W–H2W1···O5				O1W–H1W1···O3			
T(K)	d(O–H)	d(H···O)	d(O···O)	<OHO	d(O–H)	d(H···O)	d(O···O)	<OHO
260	0.908(4)	1.932(2)	2.824(5)	167.0(3)	0.913(4)	2.001(3)	2.851(5)	154.3(3)
240	0.880(4)	1.963(2)	2.830(4)	167.9(2)	0.913(4)	2.045(2)	2.848(5)	146.1(2)
220	0.892(3)	1.939(2)	2.826(4)	172.2(2)	0.916(4)	1.927(2)	2.843(5)	176.5(2)
200	0.890(3)	1.940(2)	2.826(4)	174.0(2)	0.902(3)	1.985(2)	2.843(4)	158.3(2)
180	0.924(3)	1.917(2)	2.823(4)	165.9(2)	0.904(3)	1.951(2)	2.847(4)	170.6(2)
160	0.912(3)	1.923(2)	2.824(4)	169.2(2)	0.913(3)	1.936(2)	2.840(4)	170.4(2)
140	0.901(3)	1.931(2)	2.828(4)	173.7(2)	0.902(3)	2.003(2)	2.835(4)	152.6(2)
120	0.901(3)	1.926(2)	2.826(4)	176.0(2)	0.917(3)	1.934(2)	2.836(4)	167.5(2)
100	0.936(3)	1.975(2)	2.823(4)	149.6(2)	0.938(3)	2.099(2)	2.838(4)	134.7(2)

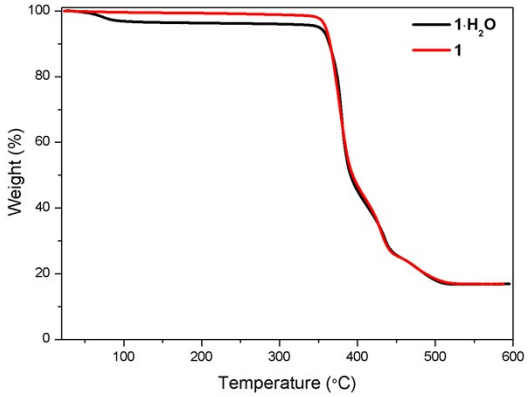


Figure S8. Thermogravimetric analysis of **1·H_2O** (black) and **1** (red).

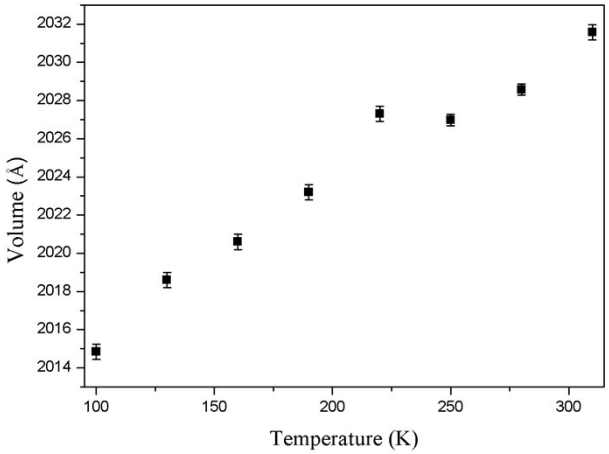


Figure S9. Variation of unit cell volume of **1** (including standard deviations) with temperature.

Table S9. List of slected angles and torsional angles in **1** in the temperature range 310 K and 100 K.

T(K)	C15··· C16···C17 (θ_2)	N1··· C12··· C18···N2 (φ_2)
310	112.5(5)	7.5(8)
280	111.8(5)	8.4(7)
250	110.7(5)	9.4(7)
220	110.6(4)	10.5(6)
190	110.0(3)	11.2(6)
160	109.7(3)	11.5(6)
130	109.6(3)	12.3(5)
100	109.2(3)	13.0(5)

Table S10. List of Screw pitch and diameter of helices in **1** in the temperature range 310 K and 100 K.

T(K)	Screw Pitch (Å)	Diameter (Å)
310	7.831(1)	11.105(5)
280	7.818(1)	11.112(5)
250	7.808(1)	11.117(5)
220	7.801(1)	11.129(4)
190	7.788(1)	11.132(4)
160	7.777(1)	11.135(4)
130	7.766(1)	11.143(4)
100	7.753(1)	11.146(4)

Table S11. List of N–H···O hydrogen bonding interactions in **1** in the temperature range 310 K and 100 K.

T(K)	d(O–H)	d(H···N)	d(O···N)	<OHN
310	0.859(4)	1.813(4)	2.643(6)	161.8(3)
280	0.859(4)	1.808(3)	2.639(5)	162.1(3)
250	0.870(4)	1.804(3)	2.641(5)	160.6(3)
220	0.869(3)	1.804(3)	2.639(5)	160.3(3)
190	0.880(3)	1.794(3)	2.637(4)	159.9(2)
160	0.880(3)	1.799(3)	2.639(4)	158.8(2)
130	0.879(3)	1.798(3)	2.637(4)	158.7(2)
100	0.880(3)	1.794(3)	2.634(4)	158.7(2)

Differential scanning calorimetry analysis

Differential scanning calorimetry (DSC) measurement was carried out at the heating rate of 10 ^{o}C min^{-1} in the temperature range of 100-310 K, under nitrogen flow of 50 mL min^{-1} on a DSC Q100 instrument. The sample was placed in an aluminum pan with a lid. An empty sealed pan was used as a reference.

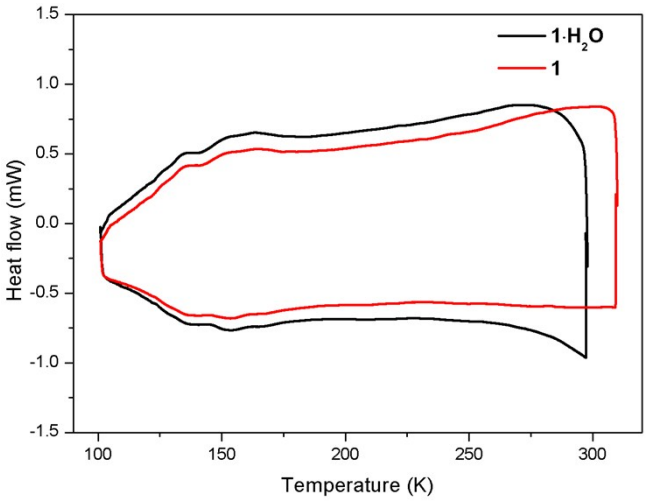


Figure S10. Differential scanning calorimetric thermogram of **1·H$_2$O** and **1**.

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