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Supporting information for

A paraelectric - ferroelectric phase transition of organically templated zinc oxalate coordination polymer

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Synthesis and crystal growth

$Zn(CH_3COO)_2$ (99%, ChemPur), $H_2C_2O_4 \cdot 2H_2O$ (99.8%, ChemPur), 1.4-diazoniabicyclo[2.2.2]octane (99.5%, Sigma-Aldrich) and agar (Fisher Scientific) were commercially available, reagent grade, and used without further purification. The growth of the metal oxalate in the presence of structure-directing organic amine (1.4-diazoniabicyclo[2.2.2]octane, denoted as DABCO) was carried out by double diffusion technique described by Henisch [1]. For this purpose, a glass U-tube of size 15 cm in length and 6 cm in diameter was used as crystallization vessel.

Agar gel solution was prepared by mixing 1.0 g of agar powder in 100 ml double distilled water at boiling. Obtained gel was poured to the U-tube and allowed to set for a 2h. Then an aqueous solution of metal salt was gently added to the first limb, while the solution of 1.4-diazoniabicyclo[2.2.2]octane and oxalic acid to the another one. The U-tube was sealed and kept undisturbed under ambient conditions. After several weeks, a needla-like, single crystals of a suitable size for X-ray analysis had formed in the gel.

Elementar anlysis

DZnOH: Found: C, 29.5; H, 4.7; N, 6.9. Calc. for $C_{10}H_{20}N_2O_{11}Zn$: C, 29.3; H, 4.9; N, 6.8 %.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) measurements of obtained crystals were performed on a DSC-7 instrument (PerkinElmer) at a rate of 20 K min^{-1} under a nitrogen atmosphere with two cycles in the temperature range 313 − 103 K.

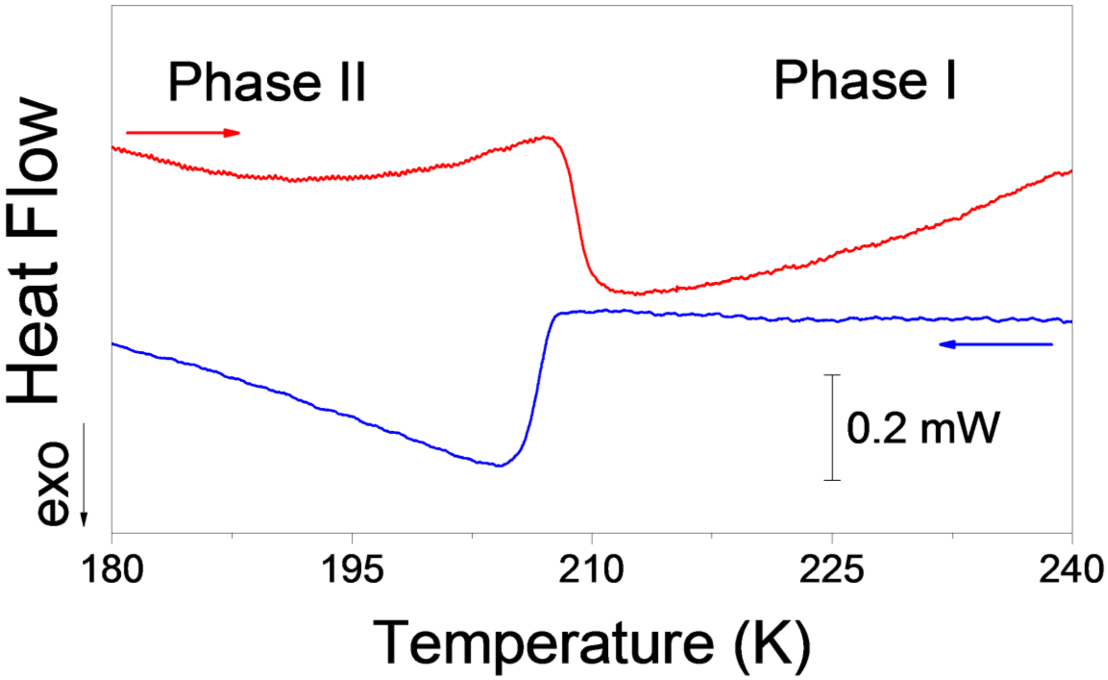

Figure S1. DSC curves (with the ramp rate of 20 K min^{-1}, sample mass 24.137 mg) for the DZnOH.

The specific heat measurements were made using a Mettler Toledo DSC-1 calorimeter, with a heating rate of 10 K min^{-1} and with a resolution of 0.4 mW.

The latent heat corresponding to the phase transition was calculated by subtraction from the data the baseline representing net specific heat. The entropy related to the phase transition was calculated by performing tabular integrations of $\int \frac{\Delta C_p}{T} dT$. The shape of the entropy (see Figure S2) and its value suggests both displacive and order-disorder contribution to the phase transition mechanism. An entropy change (ΔS) is estimated with a value of 1.5 J mol^{-1} K^{-1}. Given that $\Delta S = R \ln N$ where R is the gas constant and N is the ratio of possible atoms configuration it was found that N=1.197.

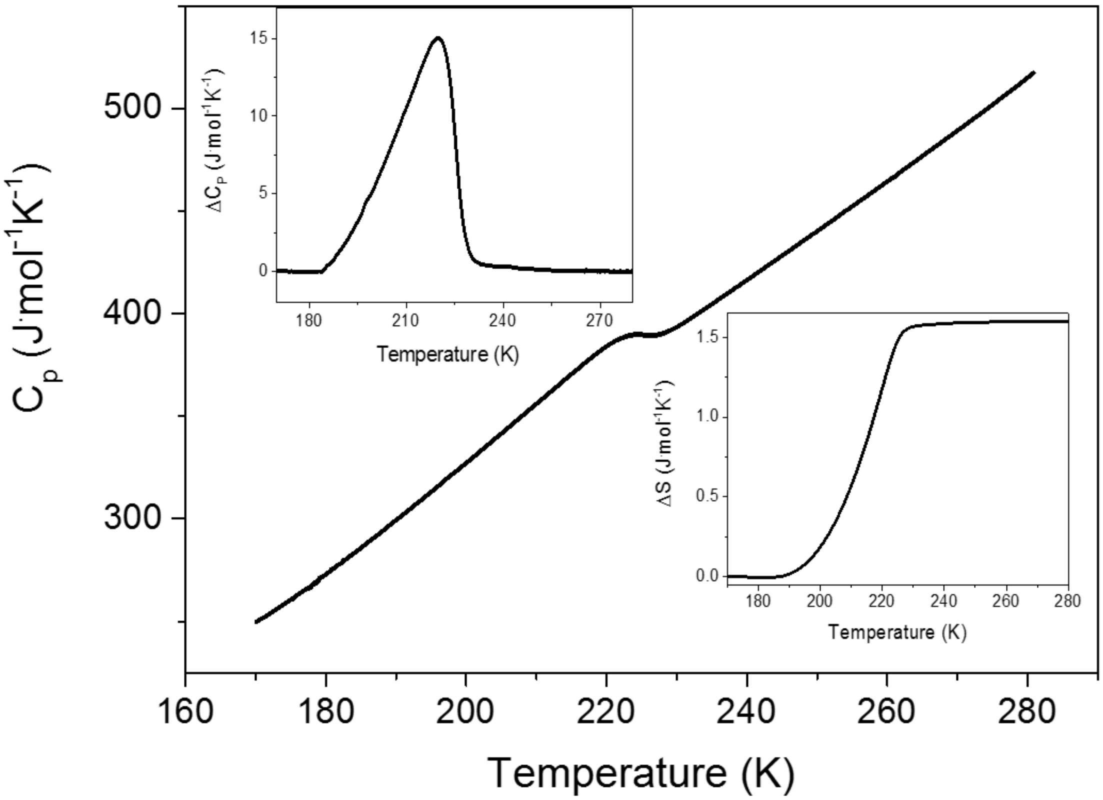

Figure S2. Specific heat of DZnOH measured in heating mode. The insets show the latent heat (ΔC_p) and entropy ΔS related to the phase transition

The calculated polarization P_{cal} (Figure S3) is about 5 times greater than the polarization value estimated from both pyroelectric and spontaneous polarization measurements. The discrepancies can result from a worse quality of crystal sample used in the pyroelectric and spontaneous polarization measurements or/and the investigated crystals were not fully monodomain.

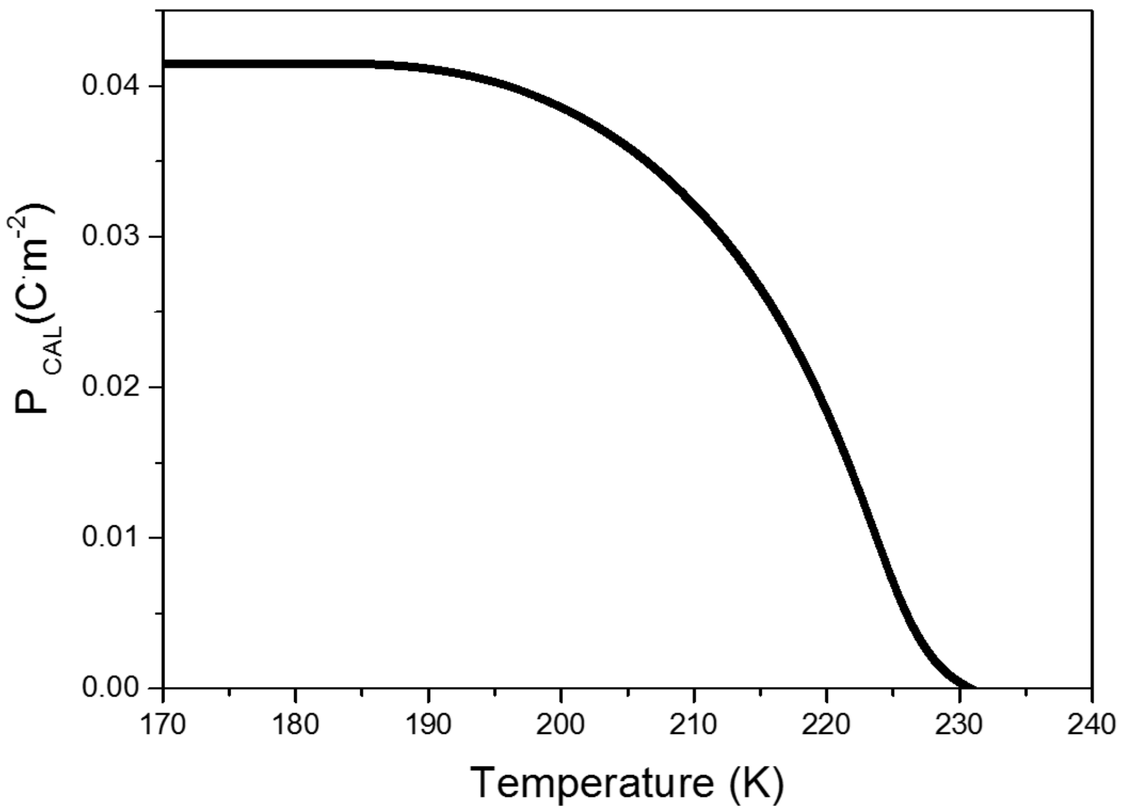

Figure S3. Temperature dependence of the spontaneous polarization calculated from $P_s^2(T) = \int \frac{2\Delta Cp}{\alpha T} dT$

Thermogravimetric analysis

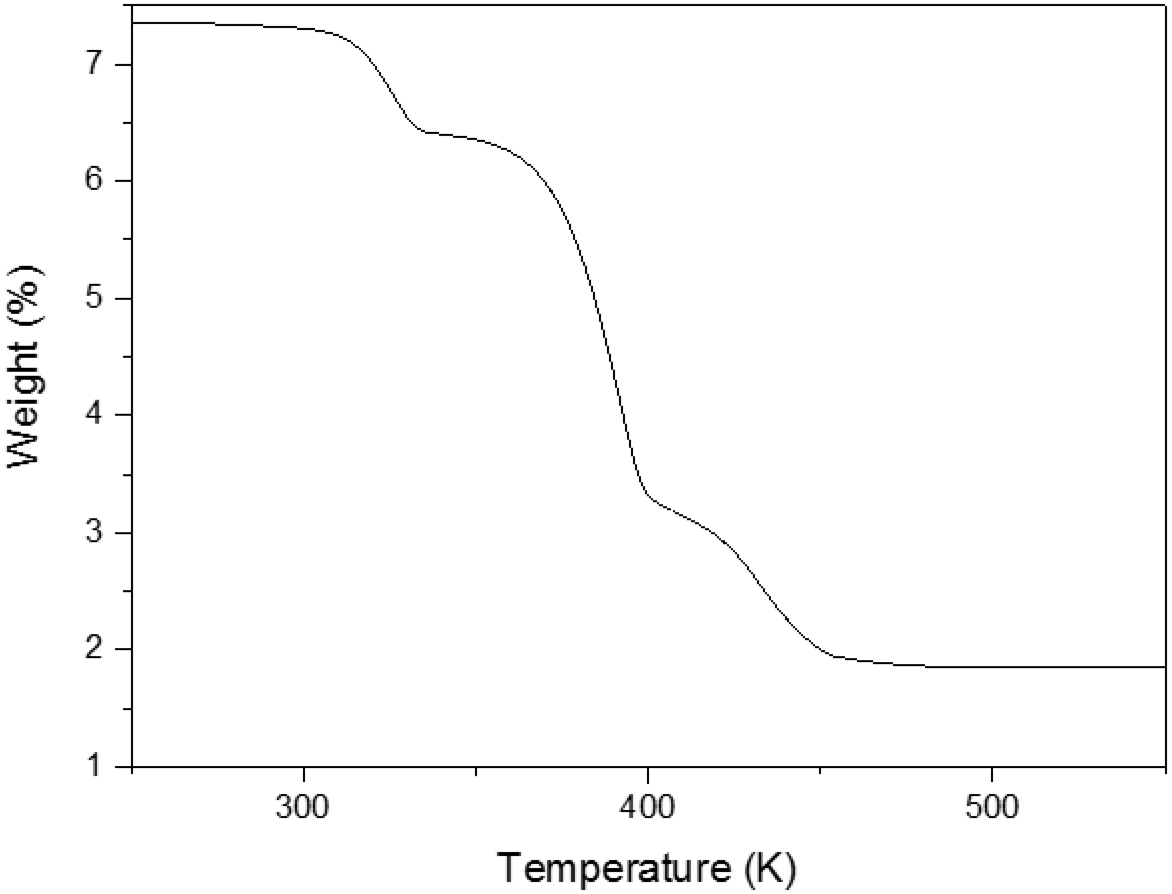

Figure S4. Thermogravimetric analysis (with the ramp rate of 10 K min^{-1}, sample mass 8.331 mg) for the DZnOH.

Table S1. Thermogravimetric analysis.

		DZnOH
3H_2O	Calculated	13.20 %
	Observed	11.78 %
3CO_2 + CO, H_2dabco	Calculated	66.24 %
	Observed	64.21 %
MeO	Calculated	19.87 %
	Observed	23.14 %

Dielectric studies

The complex dielectric permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ was measured using an Agilent 4284A Precision LCR meter in the frequency range between 100 Hz and 2 MHz and in the temperature range from

100 to 300 K. The overall error was less than 5%. Silver electrodes were sticked on the opposite faces. The dielectric measurements were carried in a controlled atmosphere (N_2).

Pyroelectric current was measured by Keithley 617 Electrometer. The spontaneous polarization was obtained by a numerical integration of the current *vs*. time curve and dividing by the sample area. In order to check the effect of external electric field on the value and orientation of the spontaneous polarization vector, DCV supply was used. The experiment was performed in such a way that the sample was first polarized in the phase I and then cooled below 207 K. After half an-hour of shorting the sample, the pyroelectric current was measured on heating. We used the electric field intensity as large as ±5 kV cm^{-1} in the first and second experiment, respectively.

Ferroelectric hysteresis loops measurements were performed using a homemade high precision set-up base on Diamand-Drenck-Pepinsky (DDP) bridge.

Powder X-Ray Diffraction

The phase purity of title compound was confirmed by powder X-ray diffraction (XRD). The diffraction pattern was collected in the reflection mode at Bragg–Brentano geometry in 2-theta range from 5 to 50 with a scan step of 0.026 deg during 1 h. An X'Pert PRO X-ray diffraction system with CuK_α radiation equipped with a PIXcel ultra-fast line detector, focusing mirror and Soller slits for $Cu\ K_{\alpha 1}$ radiation (λ = 1.54056 Å) was used (see Figure S3).

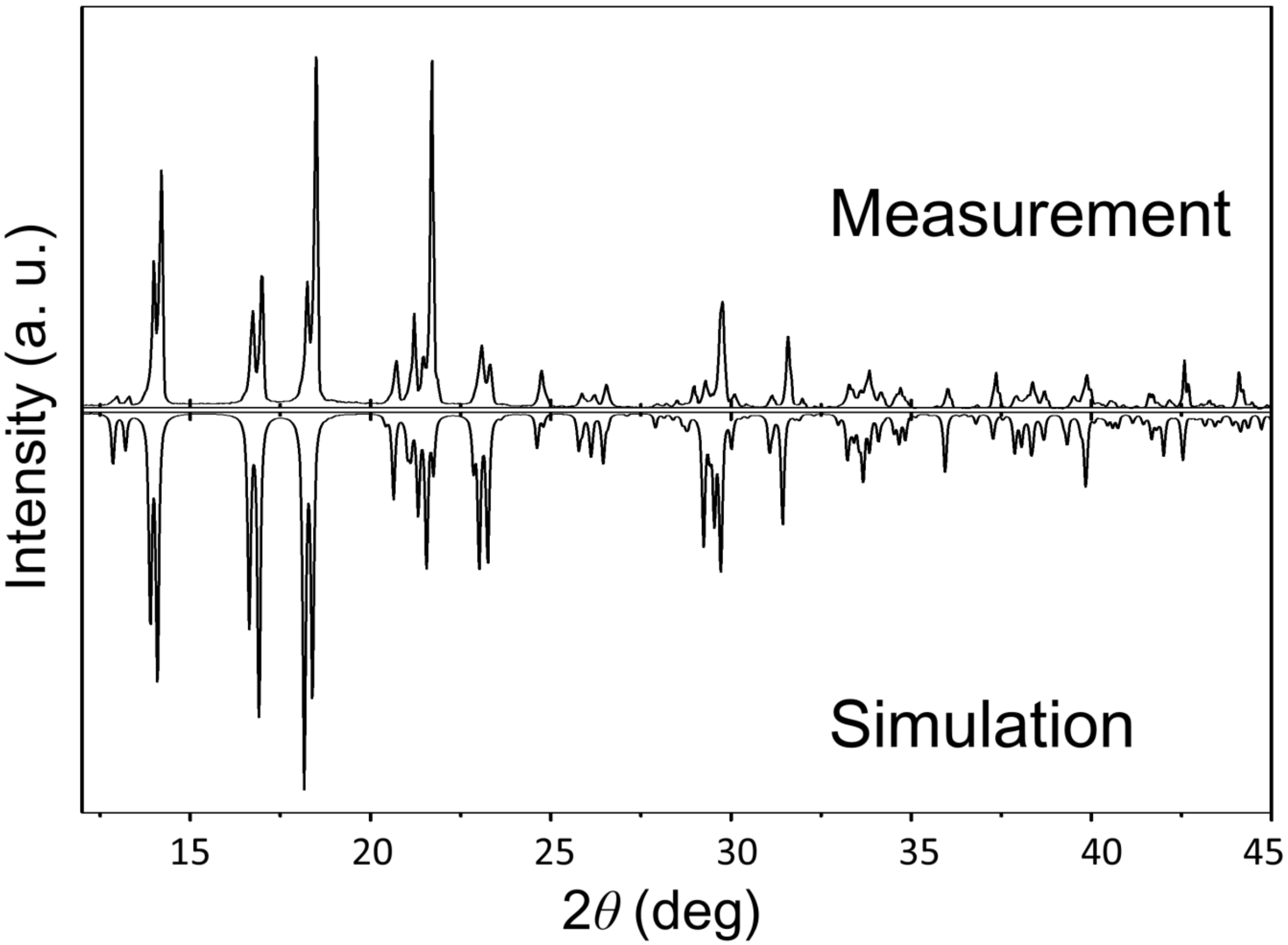

Figure S5. Powder XRD patterns for the as-prepared bulk sample DZnOH (up) together with the calculated ones based on the single crystal structure at room temperature (down).

Single-crystal X-ray diffraction

A suitable single crystal for a good data collection was selected under a polarized light microscope and glued onto a thin glass fibre by two-part epoxy adhesive. Single-crystal X-ray diffraction data were collected in wide temperature range, 100–300 K using an Xcalibur Atlas four-circle diffractometer equipped with a two-dimensional CCD detector. The graphite monochromated MoKα radiation (λ = 0.71073 Å) was used.

The data frames were reduced and corrected for absorption effects using the CrysAlisPro RED software version 1.171.38.34a (Oxford Diffraction). Final unit cell parameters were determined by least squares refinement of reflections from the data set. Direct methods structure solution, difference Fourier calculations, and full-matrix least squares refinement against F^2 were performed with SHELXS and SHELXL-2014/7 using OLEX 2.52 software.

Hydrogen atoms were placed in geometric positions (C–H ~ 0.97 Å, N–H ~ 0.91 Å and O–H ~ 0.85 Å) and treated as riding atoms. The isotropic atomic displacement parameters of the H atoms, U_{iso}(H) were set to be equal to 1.2 times the thermal parameters of the corresponding parent atoms, 1.2 U_{eq}. Water H atoms were located firstly in a difference Fourier map and were then fixed, with O–H ~ 0.85 Å and U_{iso}(H) = 1.5 U_{eq}(O).

The details of selected data collection and refinement parameters along with the crystal description are briefly summarized in Table S3.

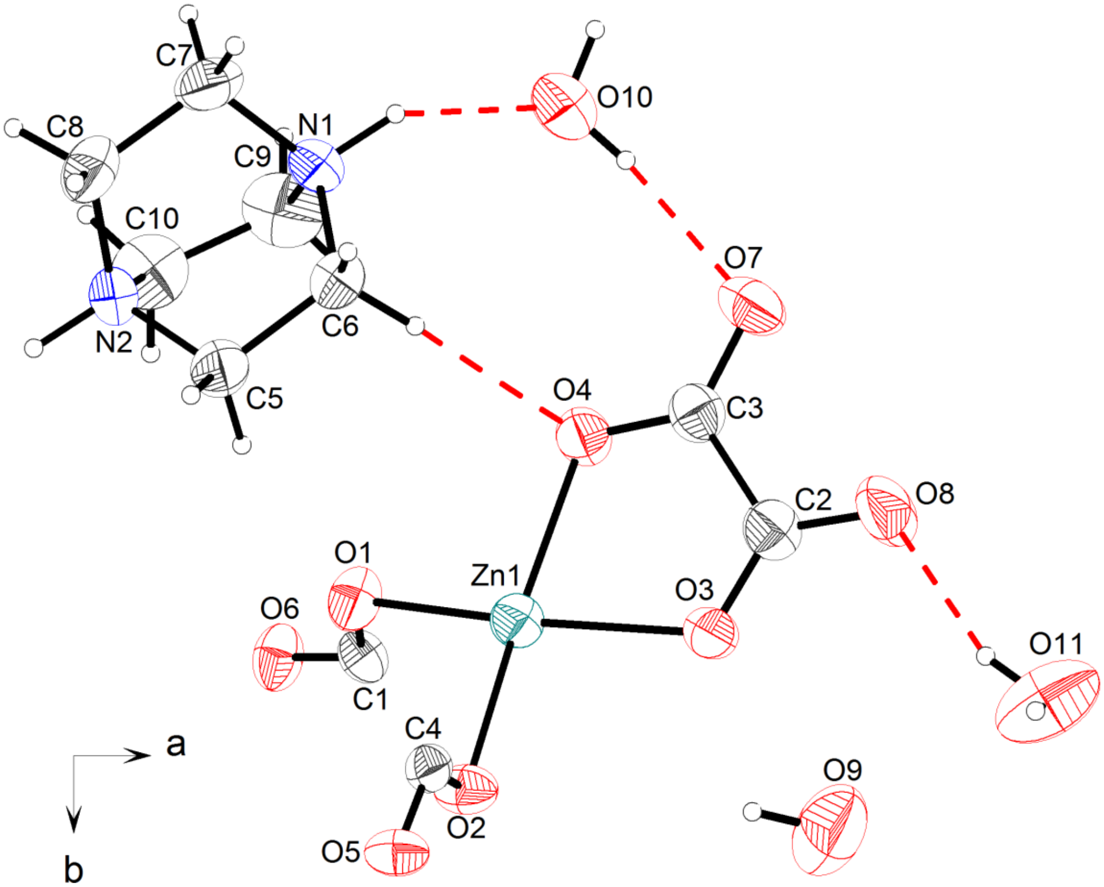

Figure S6. The asymmetric unit cell of phase I, showing the atom-numbering scheme. The labels of hydrogen atoms were omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are denoted by red dashed lines.

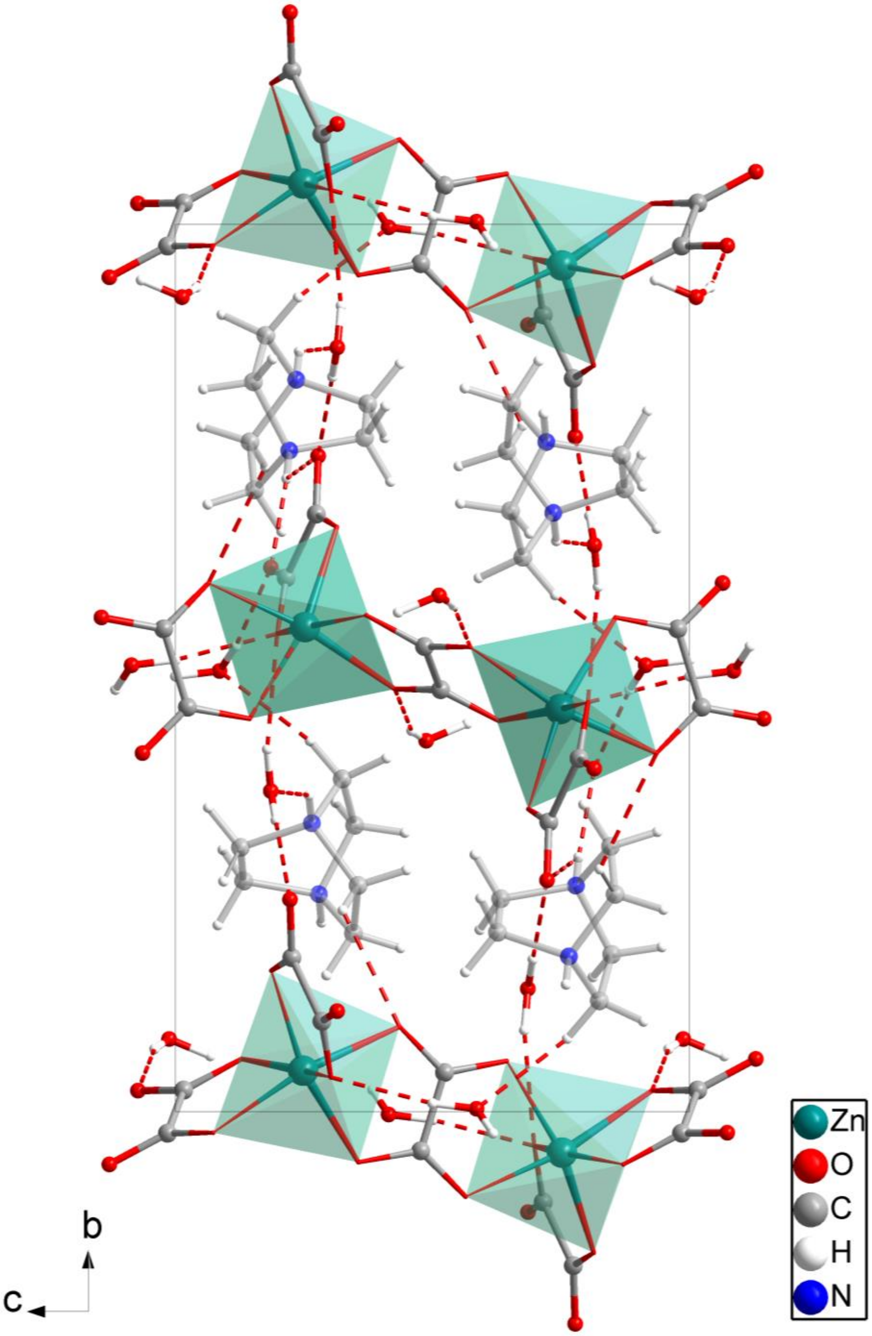

Figure S7. Packing diagram for phase I viewed along [100] showing the three-dimensional hydrogen bonded network (red dashed lines). Colour key: [ZnO_6] – cyan, oxygen – red, nitrogen – blue, carbon – grey, hydrogen – white.

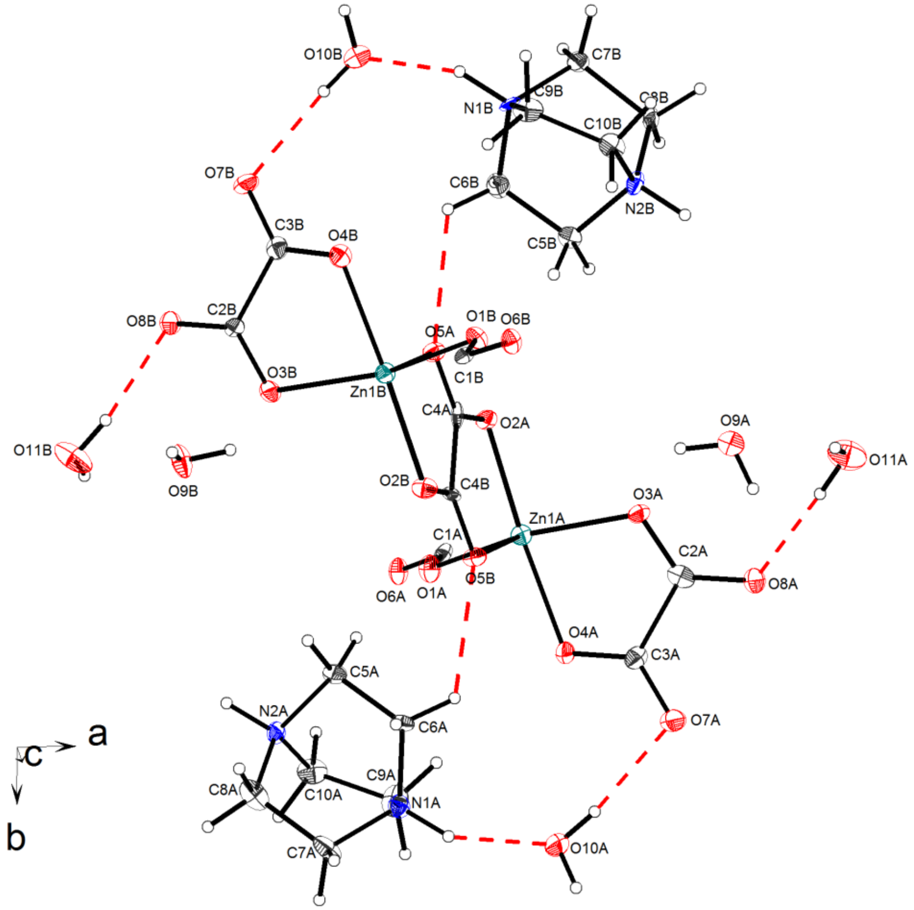

Figure S8. The asymmetric unit cell of phase II, showing the atom-numbering scheme. The labels of hydrogen atoms were omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are denoted by red dashed lines.

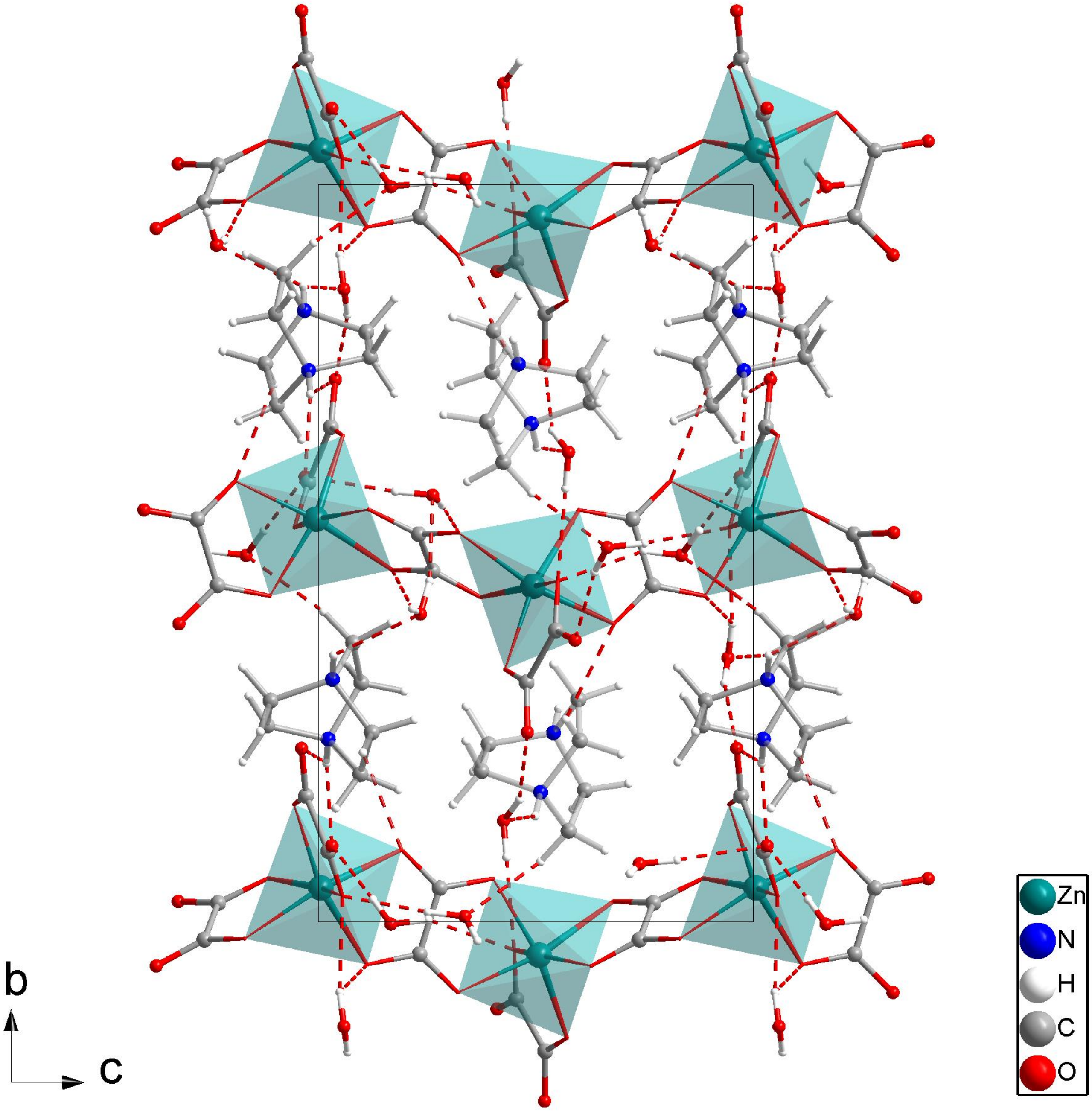

Figure S9. Packing diagram for phase II viewed along [100] showing the three-dimensional hydrogen bonded network (red dashed lines). Colour key: [ZnO_6] – cyan, oxygen – red, nitrogen – blue, carbon – grey, hydrogen – white.

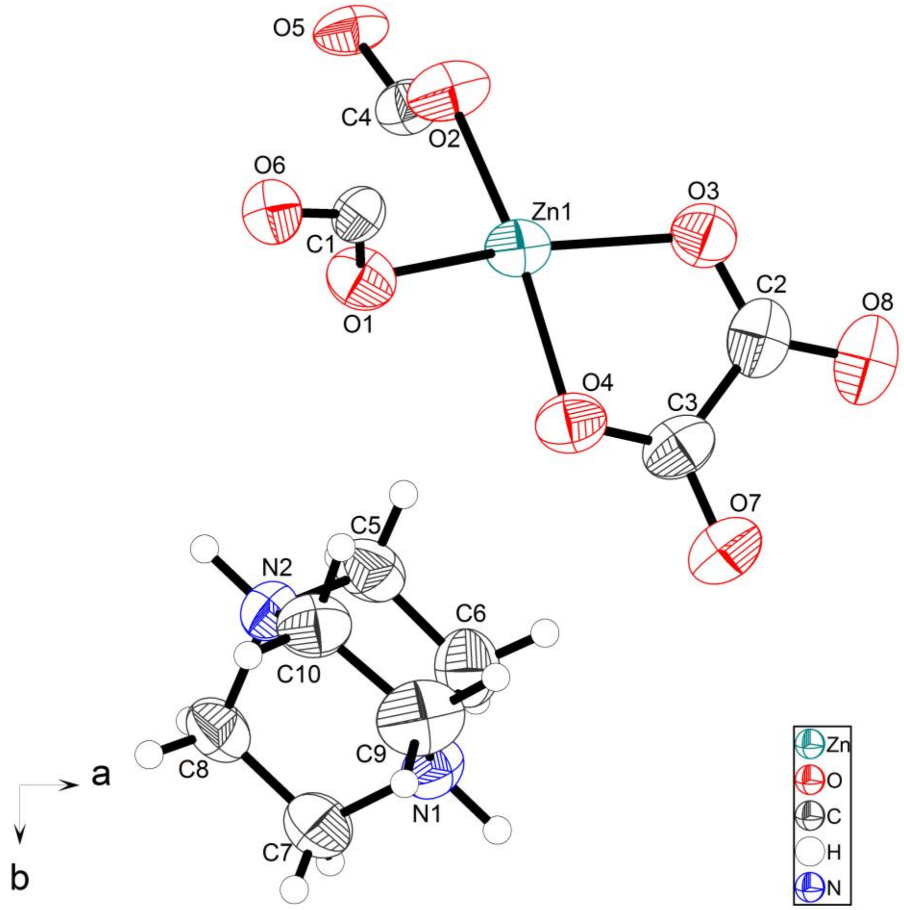

Figure S10. The asymmetric unit cell of $(DABCOH_2)[Zn(C_2O_4)_2]$ (DZnO), showing the atom-numbering scheme. The labels of hydrogen atoms were omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

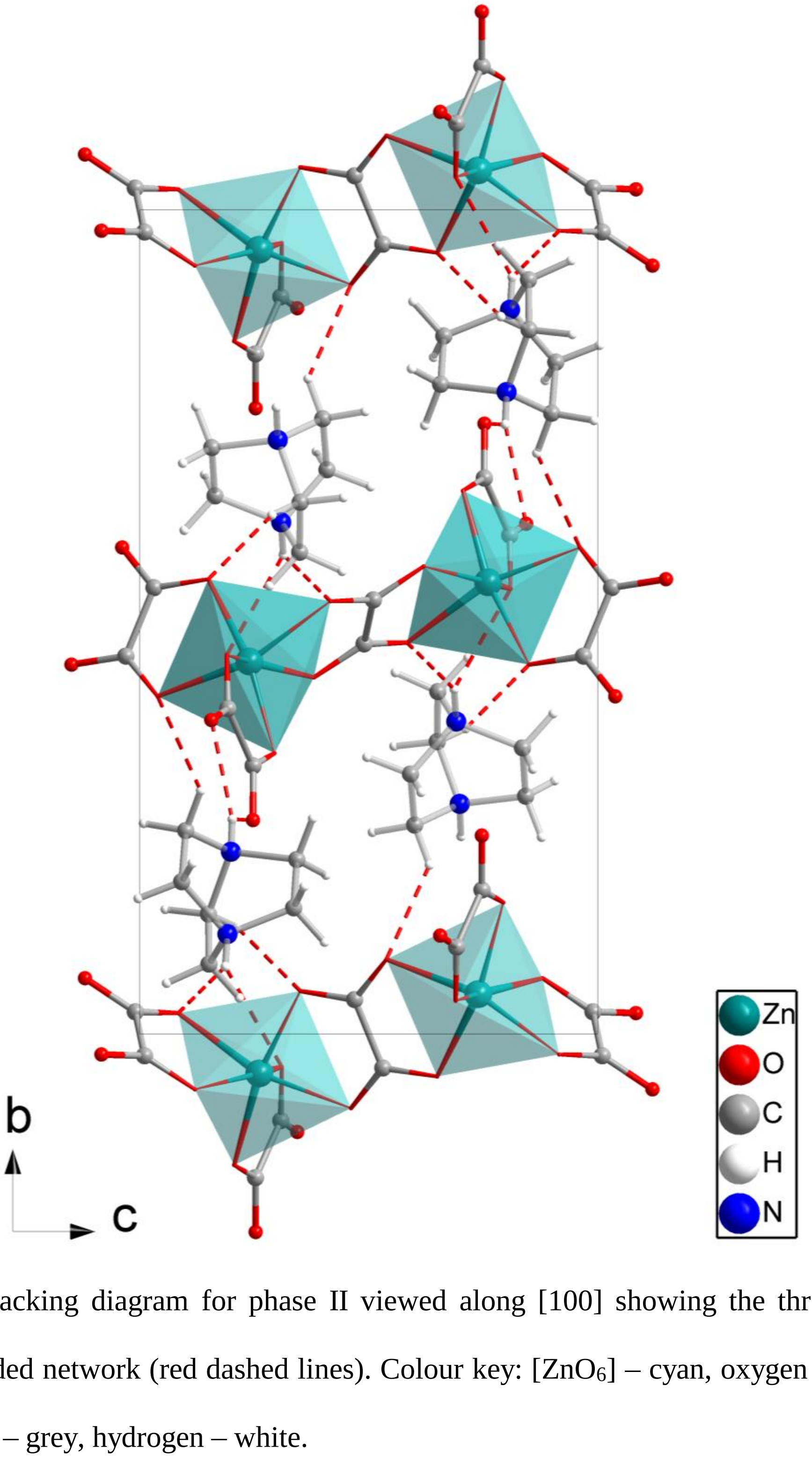

Figure S11. Packing diagram for phase II viewed along [100] showing the three-dimensional hydrogen bonded network (red dashed lines). Colour key: [ZnO_6] – cyan, oxygen – red, nitrogen – blue, carbon – grey, hydrogen – white.

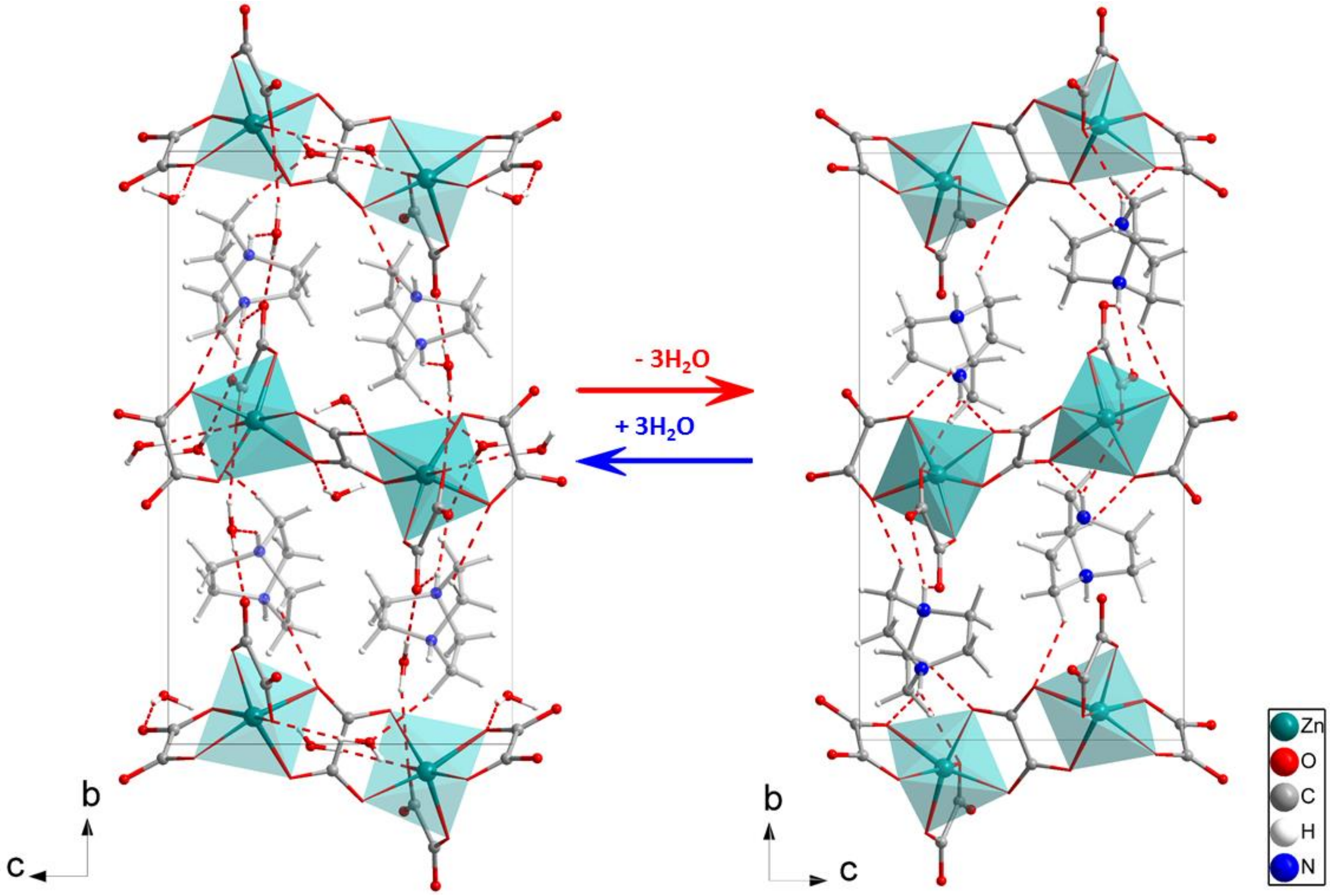

Figure S12. Schematic illustration of the single-crystal to single-crystal transformation between DZnOH and DZnO viewed along [100]. Colour key: [ZnO_6] – cyan, oxygen – red, nitrogen – blue, carbon – grey, hydrogen – white.

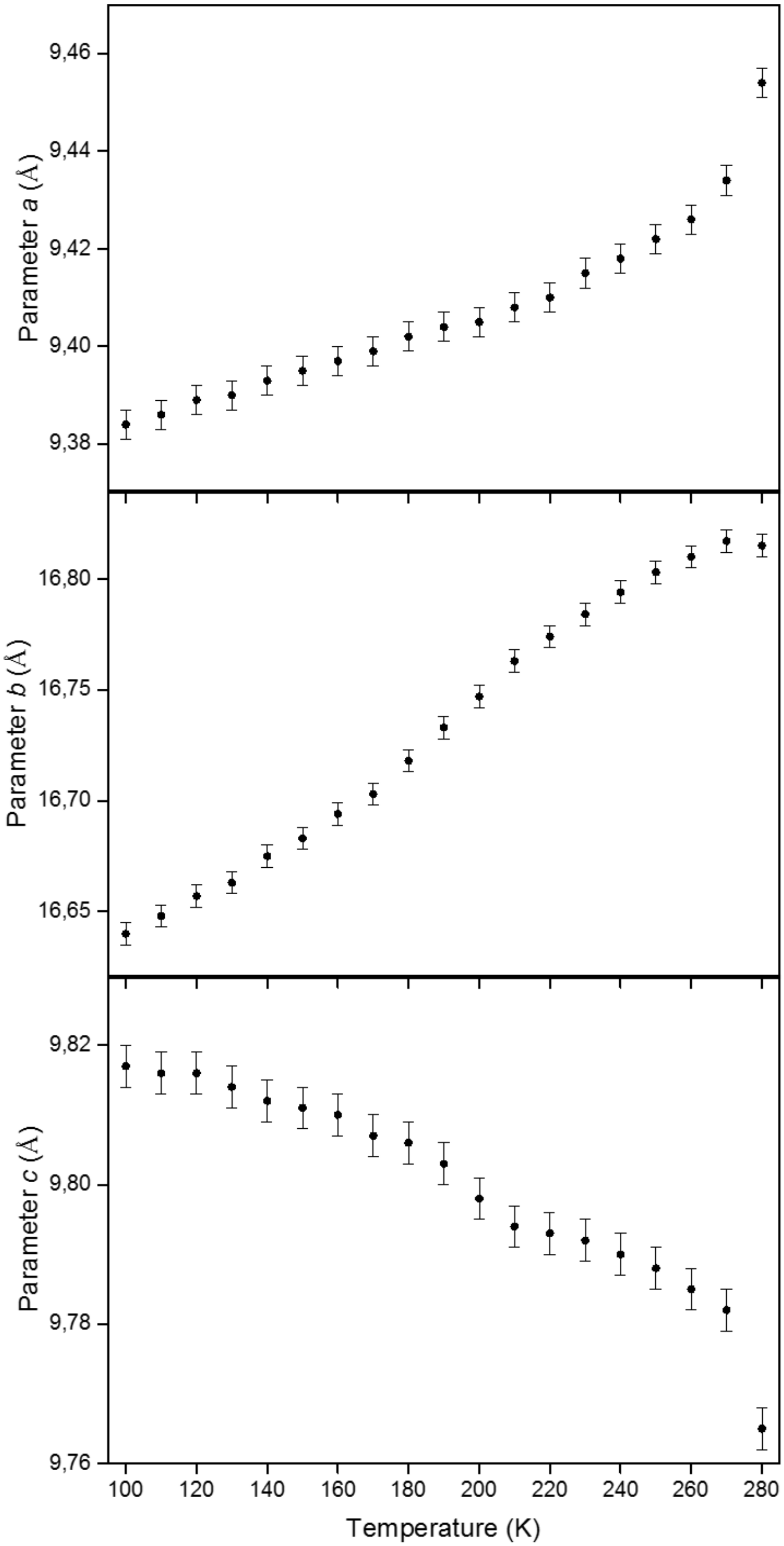
Parameter *a* (Å)
9,38
9,40
9,42
9,44
9,46
Parameter *b* (Å)
16,65
16,70
16,75
16,80
Parameter *c* (Å)
9,76
9,78
9,80
9,82
100
120
140
160
180
200
220
240
260
280
Temperature (K)

Figure S13. Thermal evolution of the monoclinic unit cell dimensions in DZnOH single crystal during heating.

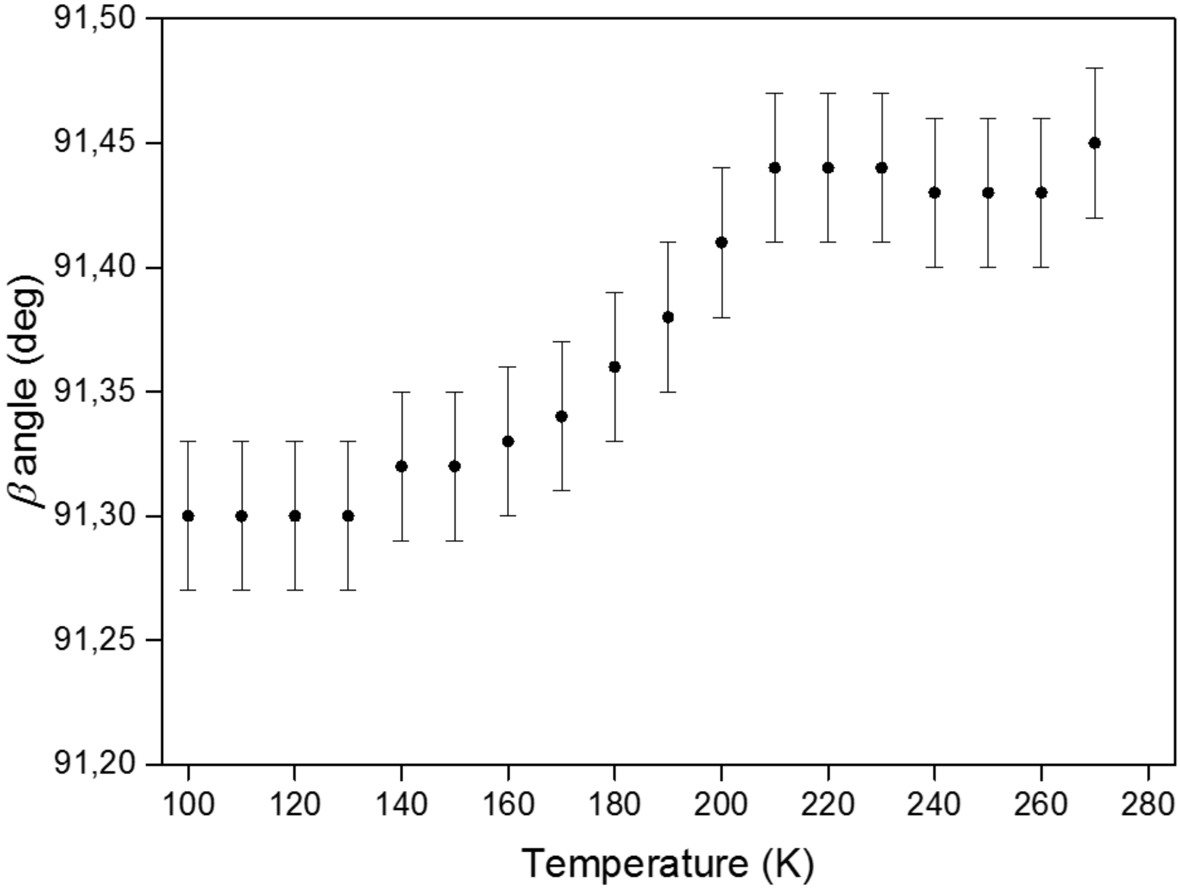

Figure S14. Thermal evolution of the monoclinic beta (β) angle in DZnOH single crystal during heating.

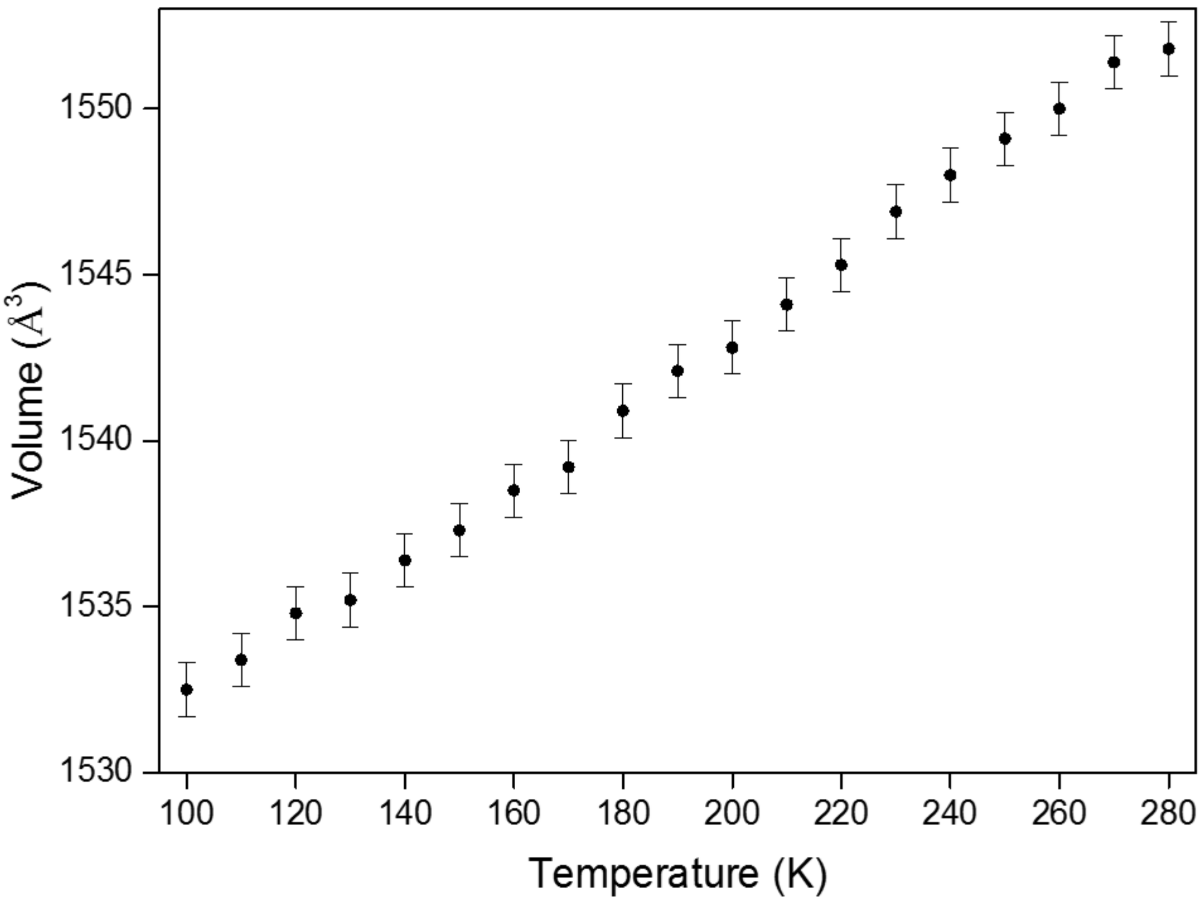

Figure S15. Thermal evolution of the unit cell volume in the DZnOH single crystals during heating.

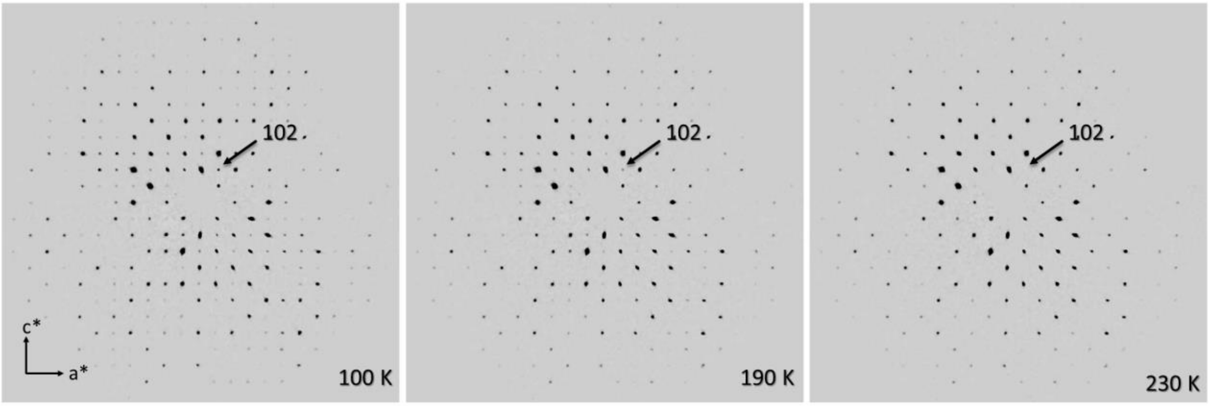

Figure S16. A reconstructed view of the *h*0*l* plane of reciprocal space for DZnOH at 100, 190 and 230 K. The appearance of diffraction intensity at reciprocal lattice below 200 K with reflection condition (*h* + *l* = 2*n* + 1) which arise due to loss of the *n* glide plane perpendicular to *b* axis.

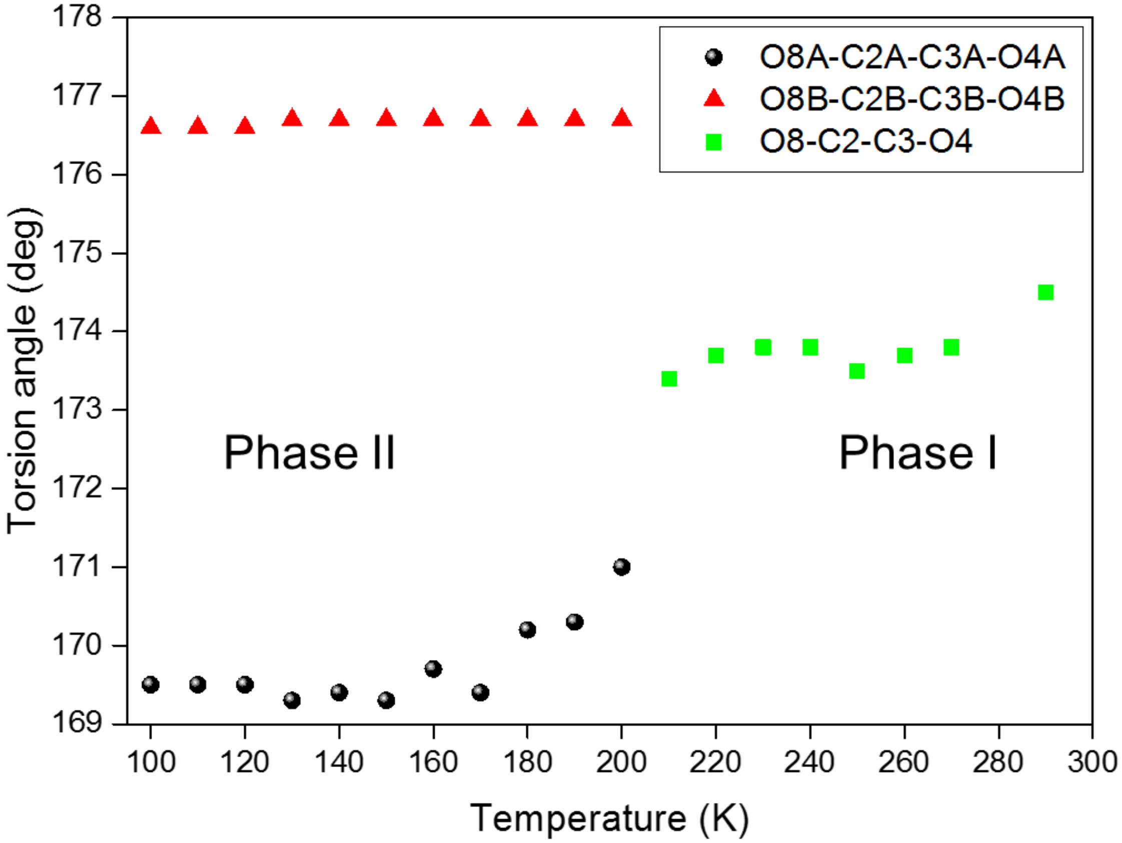

Figure S17. Torsion angle (O8–C2–C3–O4 for phase I, O8A–C2A–C3A–O4A and O8B–C2B–C3B–O4B for phase II) as a function of temperature in the DZnOH molecule.

Table S2. Atomic displacements from the high temperature phase positions.

Atom	ux	uy	uz	|u|
Zn11	-0.0035	0.0007	0.0057	0.0666
Zn12	0.0002	-0.0001	0.0070	0.0685
O11	-0.0044	0.0015	0.0057	0.0748
O12	-0.0020	0.0007	0.0057	0.0604
O21	-0.0055	0.0007	0.0064	0.0830
O22	-0.0003	-0.0011	0.0059	0.0609
O31	-0.0057	0.0006	0.0019	0.0585
O32	-0.0045	-0.0027	0.0026	0.0677
O41	-0.0029	0.0008	0.0069	0.0747
O42	-0.0017	0.0009	0.0077	0.0791
O51	-0.0050	0.0012	0.0055	0.0752
O52	-0.0020	-0.0005	0.0064	0.0664

O61	-0.0020	0.0003	0.0070	0.0714
O62	-0.0023	0.0032	0.0027	0.0641
C11	-0.0031	0.0004	0.0054	0.0616
C12	-0.0041	0.0006	0.0045	0.0600
C21	-0.0062	-0.0017	-0.0103	0.1182
C22	-0.0071	-0.0055	-0.0115	0.1597
C31	-0.0059	-0.0016	-0.0036	0.0705
C32	-0.0056	-0.0030	-0.0041	0.0827
C41	-0.0043	0.0017	0.0061	0.0785
C42	-0.0020	-0.0002	0.0053	0.0554
O71	-0.0098	-0.0038	-0.0096	0.1447
O72	-0.0117	-0.0027	-0.0099	0.1520
O81	-0.0132	-0.0045	-0.0283	0.3096
O82	-0.0145	-0.0092	-0.0316	0.3695
O91	-0.0073	-0.0038	0.0012	0.0943
O92	-0.0061	0.0005	0.0019	0.0619
O101	-0.0074	-0.0014	0.0093	0.1183
O102	-0.0106	-0.0022	0.0066	0.1260
O111	-0.0111	0.0036	0.0008	0.1214
O112	-0.0180	-0.0005	0.0021	0.1719
N11	-0.0031	0.0013	0.0068	0.0767
N12	-0.0058	0.0039	0.0140	0.1619
N21	-0.0074	0.0017	-0.0103	0.1244
N22	-0.0023	0.0020	-0.0062	0.0724
C51	0.0011	0.0038	-0.0022	0.0685
C52	0.0003	-0.0016	-0.0003	0.0274
C61	0.0041	0.0010	0.0049	0.0635
C62	0.0024	0.0012	0.0178	0.1761
C71	-0.0013	-0.0026	0.0039	0.0590
C72	0.0011	0.0032	0.0028	0.0608
C81	0.0000	0.0008	-0.0142	0.1393
C82	0.0035	0.0009	-0.0008	0.0369
C91	-0.0149	0.0040	0.0033	0.1601
C92	-0.0187	0.0011	0.0085	0.1975
C101	-0.0192	0.0021	-0.0074	0.1967
C102	-0.0120	0.0044	-0.0031	0.1377

24.07.2017 Symmetry mode analysis

http://www.cryst.ehu.es/cgi-bin/cryst/programs/nph-amplimodes 7/8

NOTE: ux, uy and uz are given in relative units. |u| is the absolute distance given in Å.

Table S3. Detailed crystallographic data for hydrous, DZnOH and anhydrous, DZnO zinc oxalate.

Chemical formula	$C_{20}H_{40}N_4O_{22}Zn_2$	$C_{10}H_{20}N_2O_{11}Zn$	$C_{10}H_{14}N_2O_8Zn$
$\boldsymbol{M_r}$	819.30	409.65	355.60
Crystal system, space group	Monoclinic, $P2_1$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
Temperature (K)	100	250	300
***a*, *b*, *c* (Å)**	9.384 (3) 16.640 (5) 9.817 (3)	9.422 (3) 16.803 (5) 9.788 (3)	7.638 (3) 17.163 (5) 9.524 (3)
β (°)	91.30 (3)	91.43 (3)	93.32 (3)
$\boldsymbol{V}$ **($Å^3$)**	1532.5 (8)	1549.1 (8)	1246.4 (7)
Z	2	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	1.67	1.65	2.02
Crystal size (mm)	0.28 × 0.18 × 0.13	0.28 × 0.18 × 0.13	0.30 × 0.18 × 0.14
Diffractometer	Xcalibur, Atlas	Xcalibur, Atlas	Xcalibur, Atlas
Absorption correction		Analytical [2]	
$\boldsymbol{T_{min}}$, $\boldsymbol{T_{max}}$	0.709, 0.838	0.712, 0.838	0.654, 0.800
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11913, 5289, 4804	11744, 3042, 2480	8699, 2454, 1243
$\boldsymbol{R_{int}}$	0.029	0.032	0.079
($\sin \theta/\lambda)_{max}$ ($Å^{-1}$)	0.617	0.617	0.617
Range of *h*, *k*, *l*	$h = -11 \rightarrow 11$ $k = -20 \rightarrow 20$ $l = -12 \rightarrow 12$	$h = -11 \rightarrow 11$ $k = -20 \rightarrow 20$ $l = -12 \rightarrow 12$	$h = -9 \rightarrow 9$ $k = -21 \rightarrow 21$ $l = -11 \rightarrow 11$
$\boldsymbol{R[F^2 > 2\sigma(F^2)], wR(F^2), S}$	0.031, 0.068, 1.05	0.033, 0.076, 1.07	0.061, 0.140, 0.97
No. of reflections	5289	3042	2454
No. of parameters	421	202	190
No. of restrains	1		
H-atom treatment		H-atom parameters constrained	
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.37, -0.43	0.36, -0.52	0.55, -0.56
Absolute structure	Refined as a perfect inversion twin.		
Absolute structure parameter	0.5		

Table S4. The geometries of the O-H···O, N-H···O and C-H···O hydrogen bonds between the water molecules, the doubly protonated 1.4-diazabicyclo-[2.2.2]-octane and the anionic metal oxalate chains (distances, Å; angles, º) in the phase I and II of hydrous, DZnOH and anhydrous, DZnO zinc oxalate.

D*—H···*A	***D*—H (Å)**	**H···*A* (Å)**	***D*···*A* (Å)**	***D*—H···*A* (°)**
(DABCOH$_2$)[Zn(C$_2$O$_4$)$_2$]·3H$_2$O, DZnOH				
***P*2$_1$, 100 K**				
N1A—H1A···O9A^{i}	1.00	2.30	2.956 (7)	121.8
N1A—H1A···O10A	1.00	1.95	2.750 (7)	135.1
N2A—H2A···O8A^{ii}	1.00	1.94	2.759 (7)	137.8
N2A—H2A···O7A^{ii}	1.00	2.05	2.858 (6)	136.0
O9A—H9AD···O9B^{iii}	0.85	2.08	2.911 (5)	166.8
O9A—H9AC···O6B^{iv}	0.85	2.07	2.898 (6)	163.1
O10A—H10E···O3A^{i}	0.85	2.17	2.952 (6)	152.8
O10A—H10F···O7A	0.85	2.00	2.836 (7)	165.8
O11A—H11B···O8A	0.85	1.94	2.793 (6)	177.7
O11A—H11A···O3B^{v}	0.85	2.06	2.842 (6)	152.3
C6A—H6AA···O5B	0.99	2.39	3.017 (7)	120.3
C7A—H7AB···O11A^{i}	0.99	2.22	3.135 (9)	152.3
N1B—H1B···O10B	1.00	1.80	2.694 (7)	147.6
N2B—H2B···O8B^{v}	1.00	1.74	2.639 (7)	147.8
N2B—H2B···O7B^{v}	1.00	2.27	2.977 (5)	126.9
O9B—H9BC···O8A^{viii}	0.85	2.08	2.930 (6)	173.8
O9B—H9BD···O6A^{vii}	0.85	1.95	2.802 (6)	175.0
O10B—H10G···O3B^{vi}	0.85	2.11	2.958 (5)	171.7
O10B—H10H···O7B	0.85	2.02	2.819 (5)	157.6
O11B—H11C···O8B	0.85	1.95	2.791 (5)	168.5
O11B—H11D···O3A^{ii}	0.85	1.98	2.805 (5)	164.8
C6B—H6BB···O5A	0.99	2.44	2.981 (8)	113.5
C7B—H7BA···O11B^{vi}	0.99	2.27	3.085 (8)	138.8

Symmetry code(s): (i) -*x*+1, *y*+1/2, -*z*+2; (ii) *x*-1, *y*, *z*; (iii) *x*+1, *y*, *z*+1; (iv) *x*, *y*, *z*+1; (v) *x*+1, *y*, *z*; (vi) -*x*, *y*-1/2, -*z*+1; (vii) *x*, *y*, *z*-1; (viii) *x*-1, *y*, *z*-1.

***P*2$_1$/*n*, 250 K**				
N1—H1···O10	0.98	1.88	2.727 (2)	143.3
N2—H2···O7^{iv}	0.98	2.20	2.945 (2)	132.1

N2—H2···O8^{iv}	0.98	1.83	2.687 (2)	143.9
O9—H9C···O6^{i}	0.85	2.04	2.868 (3)	162.5
O10—H10D···O3^{ii}	0.85	2.19	3.001 (3)	159.4
O10—H10C···O7	0.85	1.99	2.836 (3)	172.1
O11—H11A···O3^{iii}	0.85	2.01	2.837 (3)	163.9
O11—H11B···O8	0.85	1.94	2.760 (2)	162.0
C6—H6B···O5^{v}	0.97	2.48	3.038 (2)	116.1
C7—H7A···O11^{ii}	0.97	2.31	3.167 (3)	146.4

Symmetry code(s): (i) -x, -y+1, -z+1; (ii) -x+1/2, y-1/2, -z+1/2; (iii) -x+1, -y+1, -z; (iv) x-1, y, z; (v) -x, -y+1, -z

(DABCOH$_2$)[Zn(C$_2$O$_4$)$_2$], DZnO

***$P2_1/n$*, 300 K**

C5—H5A···O5^{i}	0.97	2.28	3.073 (8)	138.2
C8—H8B···O2^{ii}	0.97	2.25	3.169 (8)	158.6
N1—H1···O3^{iii}	0.98	2.40	3.027 (7)	120.9
N1—H1···O6^{iv}	0.98	1.89	2.784 (6)	150.7
N2—H2···O7^{v}	0.98	1.96	2.741 (7)	134.9
N2—H2···O8^{v}	0.98	2.15	2.995 (7)	142.9

Symmetry codes: (i) -*x*, -*y*+1, -*z*+2; (ii) -*x*-1/2, *y*+1/2, -*z*+3/2; (iii) -*x*+1/2, *y*+1/2, -*z*+3/2; (iv) *x*+1/2, -*y*+3/2, *z*+1/2; (v) *x*-1, *y*, *z*.

Table S5. Selected bond distances (Å) and bond angles (°) in hydrous, DZnOH and anhydrous, DZnO zinc oxalate.

(DABCOH$_2$)[Zn(C$_2$O$_4$)$_2$], DZnO

Parameter	**100 K, *$P2_1/n$***	**300 K, *$P2_1/n$***
Zn–O	2.066 (2) - 2.144 (3)	2.063 (4) - 2.157 (4)
C–O	1.234 (4)-1.275 (4)	1.225 (7) - 1.274 (8)
C–N	1.488 (4) - 1.502 (4)	1.469 (7) - 1.501 (7)
C–C	1.520 (6) - 1.563 (6)	1.509 (9) - 1.544 (12)
O–Zn–O	77.43 (9) - 168.77 (11)	77.27 (15) - 168.08 (17)
O–C–O	125.2 (4) - 126.9 (4)	124.3 (7) - 128.0 (7)
N–C–C	108.3 (3) - 108.8 (3)	107.9 (5) - 109.2 (5)
O–C–C	115.4 (4) - 117.8 (4)	114.7 (6) - 117.3 (7)
C–N–C	109.7 (3) - 110.7 (3)	109.2 (5) - 111.6 (5)
Zn–O–C	112.4 (2) - 114.6 (2)	111.9 (4) - 114.5 (4)
Zn– C_2O_4–Zn (Zn···Zn)	5.461 (2) – 5.580 (2)	5.473 (2) – 5.598 (2)

(DABCOH$_2$)[Zn(C$_2$O$_4$)$_2$]·3H$_2$O, DZnOH		
Parameter	**100 K, *P*2$_1$**	**250 K, *P*2$_1$/*n***
Zn–O	2.0682 (15) - 2.143 (3)	2.079 (2) - 2.139 (2)
C–O	1.243 (6) - 1.263 (6)	1.235 (4) - 1.261 (3)
C–N	1.482 (7) - 1.514 (8)	1.480 (8) - 1.491 (3)
C–C	1.514 (9) - 1.543 (9)	1.511 (5) - 1.560 (5)
O–Zn–O	79.77 (10) - 171.89 (16)	79.20 (7) - 170.01 (7)
O–C–O	125.6 (5) - 126.6 (5)	125.5 (3) - 126.6 (3)
N–C–C	107.3 (5) - 108.7 (5)	108.1 – 108.6
O–C–C	115.18 (17) - 118.50 (17)	115.8 (2) - 117.6 (2)
C–N–C	108.4 (5) - 110.5 (4)	109.1 (..) - 110.4 (…)
Zn–O–C	112.2 (3) - 114.4 (3)	112.73 (15) - 114.19 (15)
Zn–C$_2$O$_4$–Zn (Zn···Zn)	5.428 (2) – 5.475 (2)	5.443 (2) - 5.478 (2)

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[1] Henisch, H. K., Crystals in Gels and Liesegang Rings. Cambridge University Press, Cambridge, 1988.

[2] Clark, R. C., Reid, J. S., *Acta Cryst. A*51, 1995, 887.