Supplementary Material (ESI) for Chemical Communications

Reversible ferromagnetic-antiferromagnetic transformation upon dehydration-hydration of the nanoporous coordination framework, $[Co_3(OH)_2(C_4O_4)_2]•3H_2O$

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SUPPLEMENTARY INFORMATION

Thermogravimetry

DT-TGA data were recorded on several samples of approximately 20 mg each to different maximum temperatures, and in some cases, the cycles were performed up to three times. The data is reproducible apart from a slight dependence on scan rate. The uptake of water is rather slow; for example, the cooling cycles in Figure S1 were performed overnight while full re-hydration (inset to Figure S1) occurred over five days. Heating to above 300C decomposes the samples to Co_3O_4 and thus the irreversibility (in green).

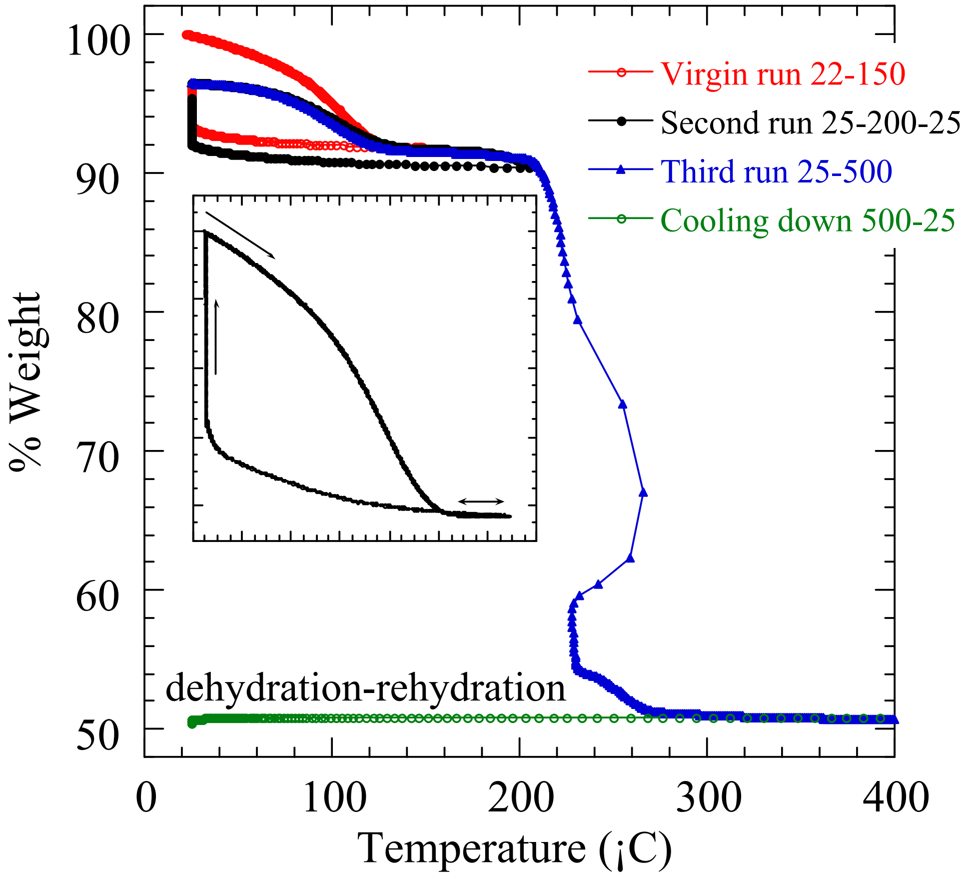


Fig. S1 TGA traces for several heating and cooling cycles. The insert shows a complete cycle of dehydration-hydration over a period of five days.

<u>Magnetic Characterisations</u>

Magnetization was measured on polycrystalline samples of approximately 10 mg each. The magnetization of the virgin sample (A.3H_2O) was first measured on cooling from 300K down to 2K in a constant field of field of 100Oe. Then ac and dc susceptibilities in a small applied field (Figure S2a) and the isothermal magnetization at 2K (Figure S3b) were recorded. The sample of then warmed to 400K and kept at this temperature for 2 hours in a helium flow, followed by further measurements of the susceptibility in 100Oe followed by the ac and dc susceptibilities as a function of frequency on cooling from 20K to 2K (Figure S2a, S2c and S2d) and the hysteresis loop at 2K. After two weeks in air the sample in air, the same procedure is performed. The results were found to be reproducible on three samples.

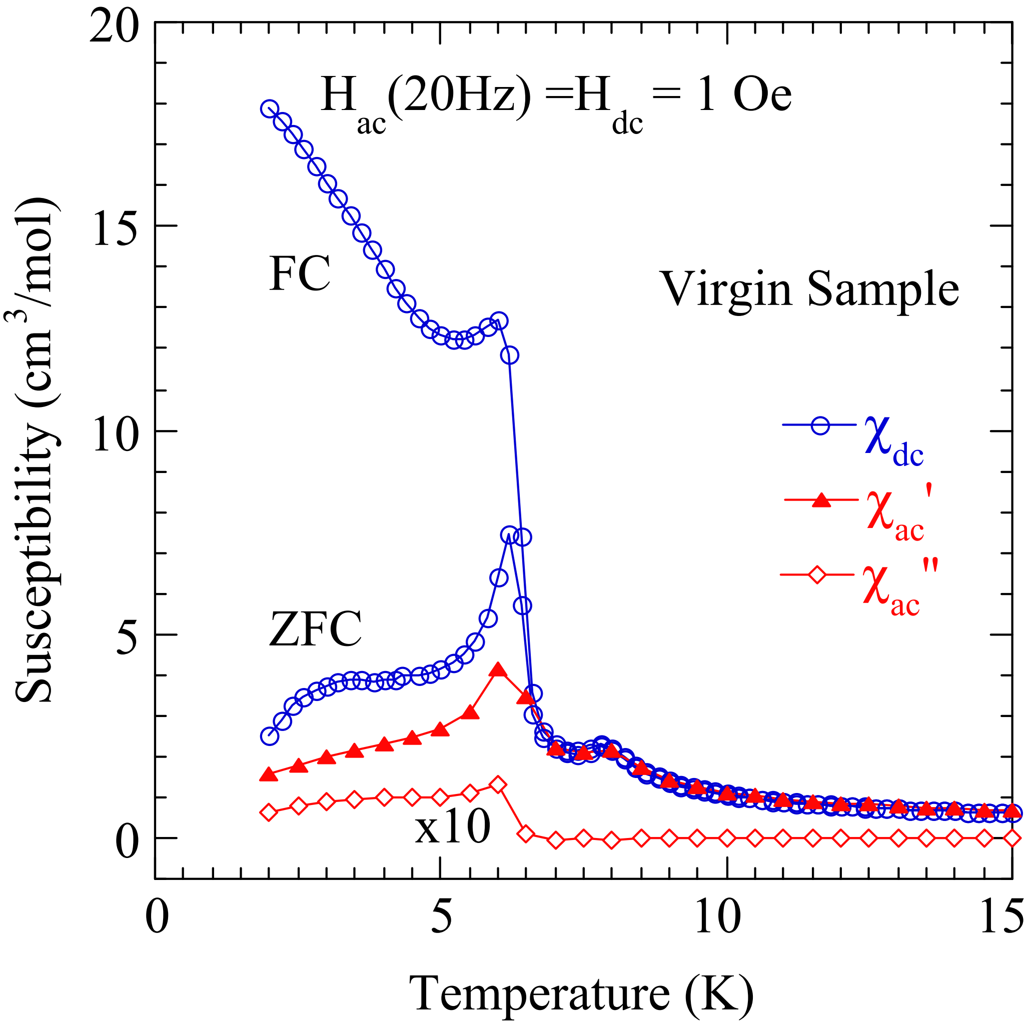


Fig S2a Temperature dependence of the ac and dc susceptibilities of the virgin sample in an applied field of 1 Oe.

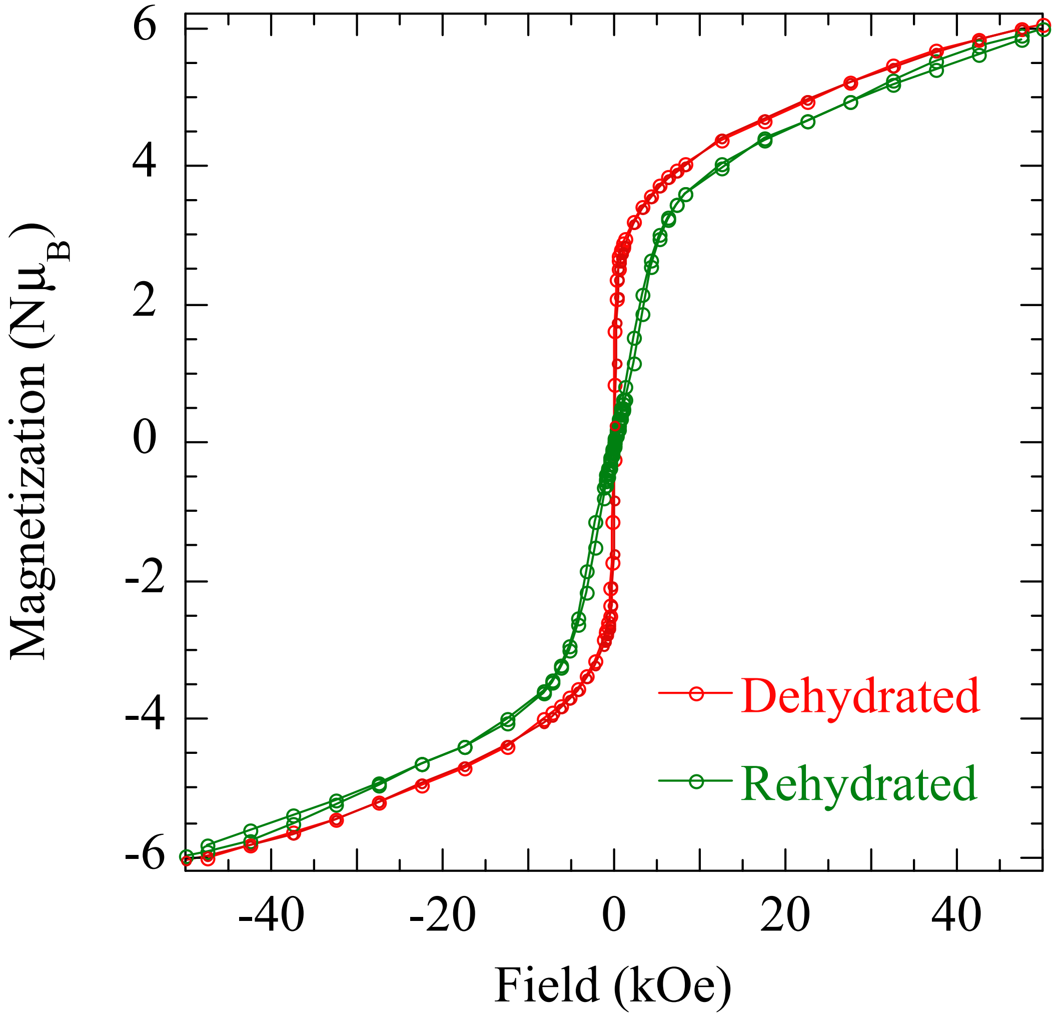


Fig S2b Field dependence of the magnetization at 2K for the de hydrated and rehydrated samples.

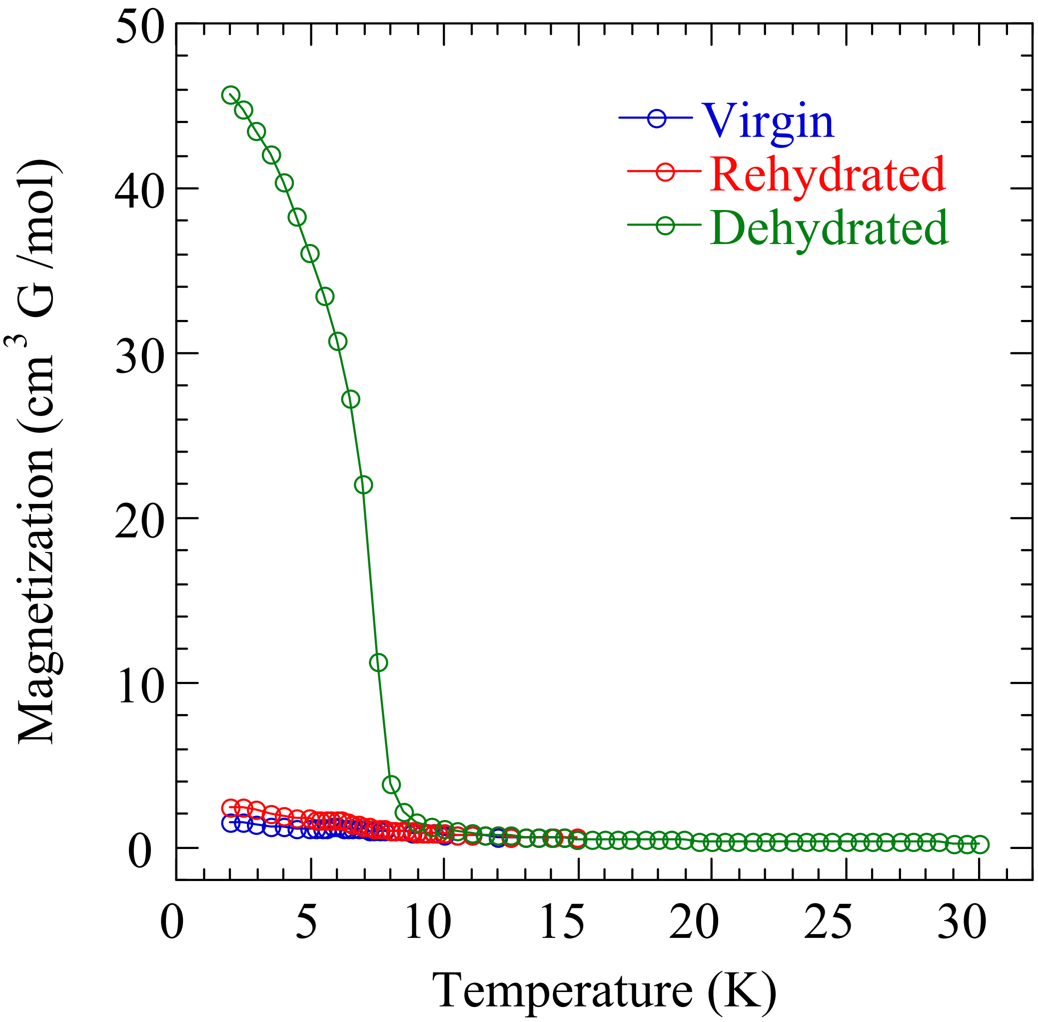


Fig S2c	Temperature dependence of the magnetization of the sample in its three states in an applied field of 1 Oe.

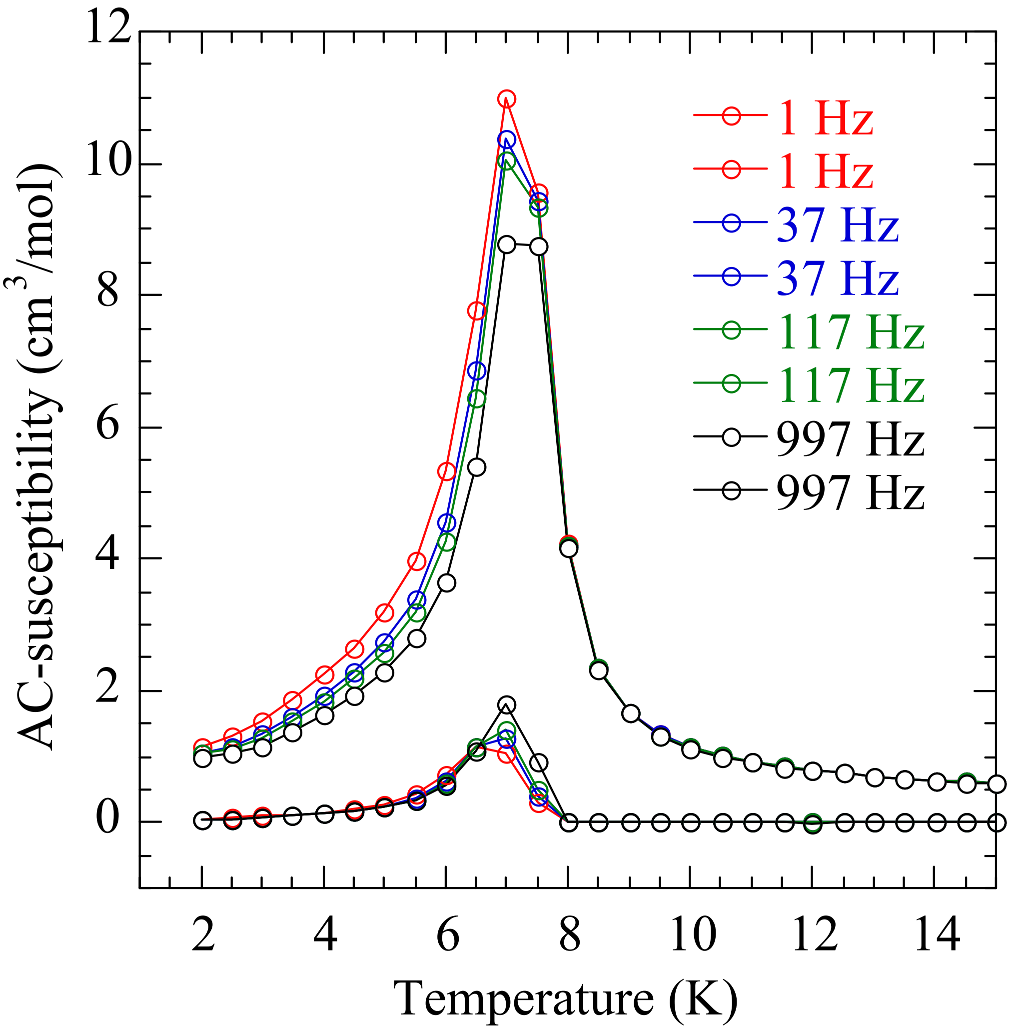


Fig S2d Temperature and frequency dependence of the ac susceptibilities of the dehydrated sample.

Single Crystal X-ray Diffraction

Single crystal X-ray diffraction (SCXRD) data for structure determination were collected on a Bruker-AXS SMART 1000 CCD diffractometer equipped with an Oxford Cryosystems Cryostream nitrogen gas stream. Single crystals were found by inspection under a polarising microscope and were attached with a thin smear of grease in a 0.3 mm diameter silica glass capillary mounted on a copper pin. For **A·3H_2O,** the pin was mounted on the goniometer and the crystal quench cooled to 150 K under the nitrogen gas stream. Diffraction patterns were generated using an incident beam of graphite monochromated Mo Kα radiation. A total of 2000 frames of intensity data (exposure time 20 s per frame) were collected over a range of incident angles covering the entire sphere. Unit cells were determined by means of 3 × 15 frames of intensity data with the exposure time 10 s. Data integration and reduction was undertaken using SAINT and XPREP. The structure was solved by direct methods and refined using SHELXL-97 and difference Fourier synthesis.

ESI amended to include the following description of the structural modelling (pg3):

The structure consists of slightly buckled brucite strips which run parallel to the *c*-axis, bridged in the *ab*-plane by the μ_4-squarate anion. This defines channels in the structure which for **A·3H_2O** contain non-coordinated guest water molecules which have extensive hydrogen bonding interactions with the framework. All non-hydrogen atoms were located from the difference map and modelled with anisotropic atomic displacement parameters. Hydrogen atoms on the hydroxide ion were located in the difference map and refined isotropically, constraining the atomic displacement parameter to be 1.2 times that of the oxygen atom. For **A·3H_2O**, the hydrogen atoms on O21 were located in the difference map and the atomic displacement parameter constrained to be 1.2 times that of the oxygen atom. This guest molecule was refined isotropically as a rigid body. No hydrogen atoms could be located for the second guest water molecule, the oxygen atom (O31) of which was refined with an isotropic atomic displacement parameter.

For *in-situ* guest desorption investigations the desorbed framework structure was determined by SCXRD on single crystals mounted with a thin smear of grease within open-ended capillary tubes such that the open end of the capillary was immersed in the nitrogen cryostream. A crystals was desolvated *in-situ* by heating from 275 K to 475 K then cooling in the nitrogen cryostream to 100 K, during which time diffraction images were collected for unit cell determinations (see Fig. S3). The full structure of the dehydrated framework **A** was determined at 100 K following the same procedure as for **A·3H_2O**. A summary of crystallographic collection and refinement data for **A·3H_2O** and **A** is given in Table S1. Full crystallographic details for these structures and an ORTEP plot of the structure of **A·3H_2O** at 150 K are given at the end of this document.

Crystallographic information files (cifs) for both structures have been deposited with the Cambridge Crystallographic Database.

Table S1 Summary of structural details for **A•3H$_2$O** and **A**.

Compound	**A•3H$_2$O**	**A**
Formula	$C_8H_2Co_3O_{10}$, H_6O_3	$C_8H_2Co_3O_{10}$
FW /gmol^{-1}	488.94	434.88
T /K	150(2)	100(2)
Space Group	$C2/m$	$C2/m$
a/Å	9.2966(10)	9.4684(11)
b/Å	12.8636(13)	12.7225(15)
c/Å	5.4998(6)	5.4873(7)
β/°	90.533(2)	90.314(2)
V/Å^3	657.68(12)	661.00(14)
Z	2	2
ρ_{calc} /Mgm^{-3}	2.469	2.185
μ /mm^{-1}	3.816	3.766
Data/restraints/parameters	810 / 0 / 64	813 / 0 / 54
R(F)/% (I>2σ(I), all data)	0.0270, 0.0325	0.0249, 0.036
R$_w$(F^2)/% (I>2σ(I), all data)	0.0617, 0.0655	0.0538, 0.0598
GOF	1.095	1.066
$d_{Co(1)-O(11)}$ /Å	2.028(2)	2.021(3)
$d_{Co(1)-O(2)}$ /Å	2.1055(17)	2.1144(18)
$d_{Co(2)-O(1)}$ /Å	2.0514(19)	2.0271(17)
$d_{Co(2)-O(11)}$ /Å	2.0545(18)	2.0739(17)
$d_{Co(2)-O(2)}$ /Å	2.1731(18)	2.1617(15)
θ[§] /°	108.3	106.7
Squarate tilt[¥] /°	23.7	22.8
O(2)-Co(1)-O(2)_#3 /°	85.81(10)	86.55(9)
O(2)-Co(1)-O(11) /°	97.34(8)	97.55(7)
O(1)-Co(2)-O(1)_#4 /°	85.38(10)	88.83(9)
O(1)-Co(2)-O(11) /°	96.37(8)	95.49(7)
O(1)-Co(2)-O(2)_#6 /°	94.05(7)	91.62(6)
O(11)-Co(2)-O(2)_#2 /°	80.47(9)	80.04(8)

#2 -x+1,y,-z+1 #3 x,-y+1,z #4 -x+1,y,-z #6 x,y,z-1

[§] θ represents the angle subtended by equivalent Co(1) atoms in neighbouring brucite chains.

[¥] Squarate tilt represents the tilt of the plane of the squarate anion away from the c-axis, defined by the angle between mean plane through the four carbon atoms of the squarate anion and a plane parallel to the c-axis and the C(2)-C(2) squarate diagonal.

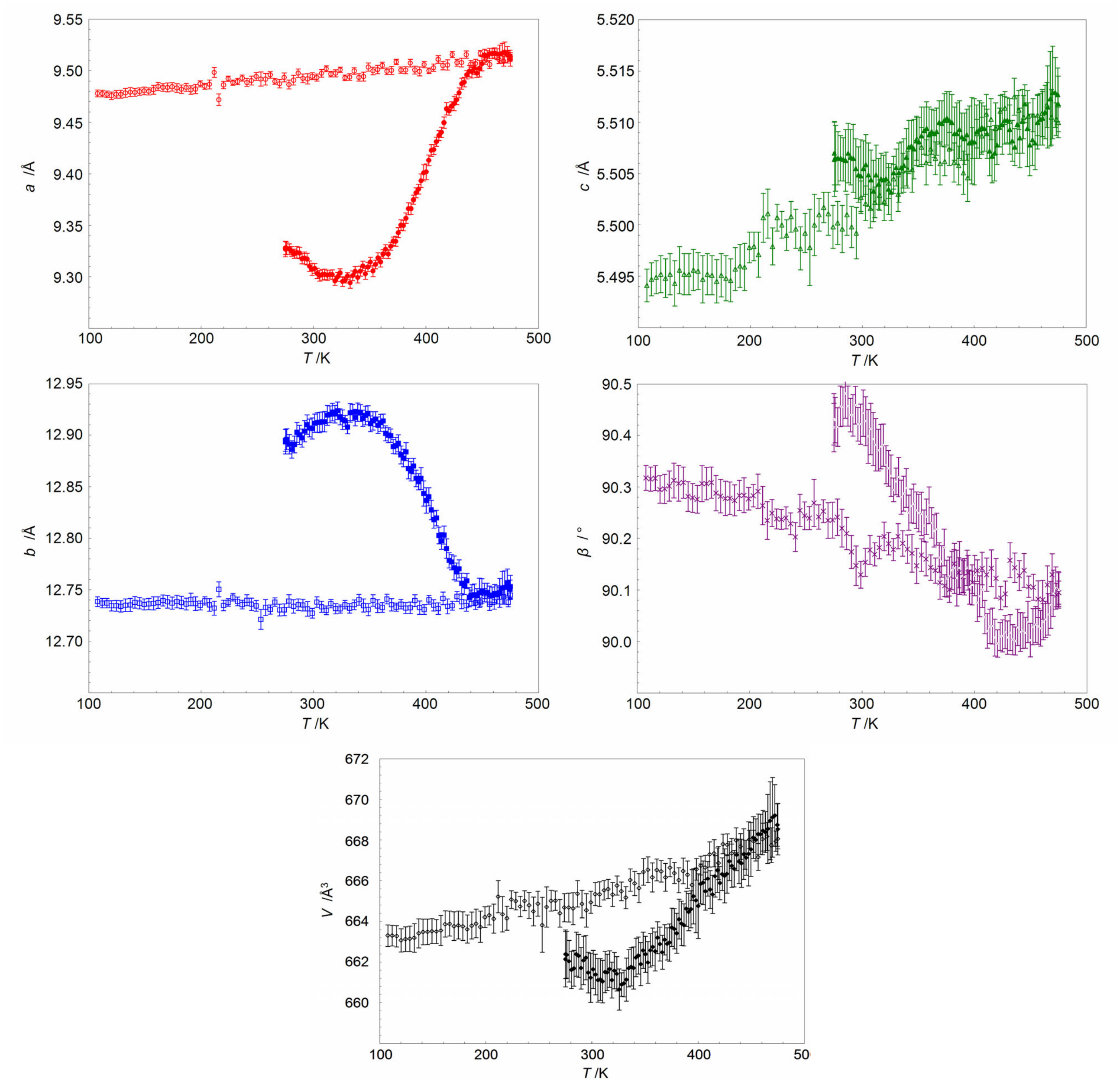


Fig. S3 **Evolution of the monoclinic unit cell parameters with heating (filled circles; dehydration of** A·3H_2O **to** A**) and cooling (open circles;** A**). Error bars are ±1 e.s.d.**

Full X-ray Crystallographic Tables

Table 1. Crystal data and structure refinement for $A\cdot3H_2O$ at 150 K.

Identification code	$A\cdot3H_2O$	
Empirical formula	C8 H8 Co3 O13	
Formula weight	488.94	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, *C*2/*m*	
Unit cell dimensions	*a* = 9.2966(10) Å	α = 90°
	b = 12.8636(13) Å	β = 90.533(2)°
	c = 5.4998(6) Å	γ = 90°
Volume	657.68(12) $Å^3$	
Z, Calculated density	2, 2.469 Mg/m^3	
Absorption coefficient	3.816 mm^{-1}	
F(000)	482	
Crystal size	0.14 x 0.09 x 0.08 mm	
Theta range for data collection	2.70 to 27.95°	
Limiting indices	$-11<=h<=11$, $-16<=k<=16$, $-7<=l<=7$	
Reflections collected / unique	6567 / 810 [*R*(int) = 0.0231]	
Completeness to theta = 27.95	97.2 %	
Absorption correction	Empirical	
Max. and min. transmission	0.737 and 0.669	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	810 / 0 / 64	
Goodness-of-fit on F^2	1.095	
Final *R* indices [*I*>2sigma(*I*)]	R_1 = 0.0270, wR_2 = 0.0617	
R indices (all data)	R_1 = 0.0325, wR_2 = 0.0655	
Largest diff. peak and hole	0.781 and -0.623 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4), equivalent isotropic displacement parameters (Å^2 x 10^4) and site occupation parameters for A·3H_2O at 150 K. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)	Occ
Co(1)	5000	5000	5000	58(2)	1000
Co(2)	5000	3799(1)	0	66(2)	1000
O(1)	3807(2)	2626(2)	1508(3)	112(4)	1000
O(11)	3979(3)	5000	1739(5)	82(5)	1000
C(1)	3098(3)	2575(2)	3415(4)	93(5)	1000
O(2)	3688(2)	3881(1)	6715(3)	91(4)	1000
C(2)	3039(3)	3121(2)	5754(4)	80(5)	1000
O(21)	1083(6)	4393(4)	999(10)	365(12)	500
O(31)	739(10)	5000	5785(17)	530(20)	500

Table 3. Bond lengths [Å] and angles [°] for A·3H_2O at 150 K.

Co(1)-O(11)#1	2.021(3)
Co(1)-O(11)	2.021(3)
Co(1)-O(2)#2	2.1144(18)
Co(1)-O(2)	2.1144(18)
Co(1)-O(2)#3	2.1144(18)
Co(1)-O(2)#1	2.1144(18)
Co(2)-O(1)#4	2.0514(19)
Co(2)-O(1)	2.0514(19)
Co(2)-O(11)	2.0545(18)
Co(2)-O(11)#5	2.0545(18)
Co(2)-O(2)#6	2.1731(18)
Co(2)-O(2)#2	2.1731(18)
O(1)-C(1)	1.246(3)
O(11)-Co(2)#5	2.0545(18)
O(11)-H(11)	0.74(5)
C(1)-C(2)#7	1.462(3)
C(1)-C(2)	1.467(3)
O(2)-C(2)	1.262(3)
O(2)-Co(2)#8	2.1731(18)
C(2)-C(1)#7	1.462(3)
O(21)-O(21)#3	1.561(11)
O(21)-H(21A)	0.8674
O(21)-H(21B)	0.8661
O(31)-O(31)#9	1.616(19)

O(11)#1-Co(1)-O(11)	180.0
O(11)#1-Co(1)-O(2)#2	97.34(8)
O(11)-Co(1)-O(2)#2	82.66(8)
O(11)#1-Co(1)-O(2)	82.66(8)
O(11)-Co(1)-O(2)	97.34(8)
O(2)#2-Co(1)-O(2)	94.19(10)
O(11)#1-Co(1)-O(2)#3	82.66(8)
O(11)-Co(1)-O(2)#3	97.34(8)
O(2)#2-Co(1)-O(2)#3	180.0
O(2)-Co(1)-O(2)#3	85.81(10)
O(11)#1-Co(1)-O(2)#1	97.34(8)
O(11)-Co(1)-O(2)#1	82.66(8)
O(2)#2-Co(1)-O(2)#1	85.81(10)
O(2)-Co(1)-O(2)#1	180.00(7)
O(2)#3-Co(1)-O(2)#1	94.19(10)
O(1)#4-Co(2)-O(1)	85.38(10)
O(1)#4-Co(2)-O(11)	174.23(9)
O(1)-Co(2)-O(11)	96.37(8)
O(1)#4-Co(2)-O(11)#5	96.37(8)
O(1)-Co(2)-O(11)#5	174.23(9)
O(11)-Co(2)-O(11)#5	82.43(11)
O(1)#4-Co(2)-O(2)#6	90.07(7)
O(1)-Co(2)-O(2)#6	94.05(7)
O(11)-Co(2)-O(2)#6	95.29(9)
O(11)#5-Co(2)-O(2)#6	80.47(9)
O(1)#4-Co(2)-O(2)#2	94.05(7)
O(1)-Co(2)-O(2)#2	90.07(7)
O(11)-Co(2)-O(2)#2	80.47(9)
O(11)#5-Co(2)-O(2)#2	95.29(9)
O(2)#6-Co(2)-O(2)#2	174.40(10)
C(1)-O(1)-Co(2)	132.21(17)
Co(1)-O(11)-Co(2)	101.41(10)
Co(1)-O(11)-Co(2)#5	101.41(10)

Co(2)-O(11)-Co(2)#5	97.57(11)
Co(1)-O(11)-H(11)	125(4)
Co(2)-O(11)-H(11)	114(2)
Co(2)#5-O(11)-H(11)	114(2)
O(1)-C(1)-C(2)#7	133.3(2)
O(1)-C(1)-C(2)	137.5(2)
C(2)#7-C(1)-C(2)	89.2(2)
C(2)-O(2)-Co(1)	128.01(16)
C(2)-O(2)-Co(2)#8	124.94(16)
Co(1)-O(2)-Co(2)#8	94.73(7)
O(2)-C(2)-C(1)#7	133.4(2)
O(2)-C(2)-C(1)	135.8(2)
C(1)#7-C(2)-C(1)	90.8(2)
O(21)#3-O(21)-H(21A)	90.6
O(21)#3-O(21)-H(21B)	148.7
H(21A)-O(21)-H(21B)	115.2

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1   #2 -x+1,y,-z+1
#3 x,-y+1,z   #4 -x+1,y,-z   #5 -x+1,-y+1,-z
#6 x,y,z-1   #7 -x+1/2,-y+1/2,-z+1
#8 x,y,z+1   #9 -x,-y+1,-z+1

Table 4. Anisotropic displacement parameters ($Å^2 \times 10^4$) for $A\cdot 3H_2O$ at 150 K. The anisotropic displacement factor exponent takes the form: $-2 \pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$

	U11	U22	U33	U23	U13	U12
Co(1)	73(3)	55(3)	47(3)	0	5(2)	0
Co(2)	92(3)	51(2)	54(2)	0	15(2)	0
O(1)	148(10)	104(9)	85(8)	-11(7)	44(7)	-27(7)
O(11)	51(12)	112(13)	83(12)	0	-9(9)	0
C(1)	100(12)	77(12)	103(11)	-1(9)	-11(9)	1(10)
O(2)	110(9)	80(9)	82(8)	-3(7)	-1(7)	-32(7)
C(2)	86(11)	85(11)	69(11)	9(9)	2(9)	-1(9)

Table 5. Hydrogen coordinates (x 10^3), isotropic displacement parameters (Å^2 x 10^3) and site occupation parameters for A·$3H_2O$ at 150 K.

	x	y	z	U(eq)	Occ
H(11)	318(6)	500	156(9)	10	1000
H(21A)	66	439	240	44	500
H(21B)	103	382	19	44	500

Table 6. Hydrogen bonds for A·$3H_2O$ at 150 K [Å and°].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(11)-H(11)...O(21)	0.74(5)	2.12(5)	2.829(6)	158.4(6)
O(11)-H(11)...O(21)#3	0.74(5)	2.12(5)	2.829(6)	158.4(6)
O(21)-H(21A)...O(31)#9	0.87	1.83	2.581(11)	144.3
O(21)-H(21A)...O(31)	0.87	2.02	2.767(10)	143.0
O(21)-H(21B)...O(1)#10	0.87	2.08	2.943(6)	171.4

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1 #2 -x+1,y,-z+1 #3 x,-y+1,z
#4 -x+1,y,-z #5 -x+1,-y+1,-z #6 x,y,z-1
#7 -x+1/2,-y+1/2,-z+1 #8 x,y,z+1 #9 -x,-y+1,-z+1
#10 -x+1/2,-y+1/2,-z

Table 7. Crystal data and structure refinement for A at 100 K.

Identification code	A
Empirical formula	C8 H2 Co3 O10
Formula weight	434.89
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, *C*2/*m*
Unit cell dimensions	*a* = 9.4684(11) Å α = 90° *b* = 12.7225(15) Å β = 90.314(2)° *c* = 5.4873(7) Å γ = 90°
Volume	661.00(14) Å^3
Z, Calculated density	2, 2.185 Mg/m^3
Absorption coefficient	3.766 mm^{-1}
F(000)	422
Crystal size	0.14 x 0.09 x 0.08 mm
Theta range for data collection	2.68 to 27.98°
Limiting indices	-12<=*h*<=11, -16<=*k*<=16, -7<=*l*<=7
Reflections collected / unique	2647 / 813 [*R*(int) = 0.0238]
Completeness to theta = 27.98	96.9 %
Absorption correction	Empirical
Max. and min. transmission	0.740 and 0.672
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	813 / 0 / 54
Goodness-of-fit on F^2	1.066
Final *R* indices [*I*>2sigma(*I*)]	R_1 = 0.0249, wR_2 = 0.0538
R indices (all data)	R_1 = 0.0360, wR_2 = 0.0598
Largest diff. peak and hole	0.466 and -0.437 e.Å^{-3}

Table 8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^4) for A at 100 K. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Co(1)	5000	5000	5000	49(2)
Co(2)	5000	3760(1)	0	56(1)
O(1)	3775(2)	2622(1)	1478(3)	85(3)
O(11)	3995(3)	5000	1726(4)	68(5)
C(1)	3081(2)	2572(2)	3396(4)	72(4)
O(2)	3731(2)	3866(1)	6723(3)	75(3)
C(2)	3054(2)	3114(2)	5760(4)	67(4)

Table 9. Bond lengths [Å] and angles [°] for A at 100 K.

Co(1)-O(11)	2.028(2)
Co(1)-O(11)#1	2.028(2)
Co(1)-O(2)	2.1055(17)
Co(1)-O(2)#2	2.1055(17)
Co(1)-O(2)#1	2.1055(17)
Co(1)-O(2)#3	2.1055(17)
Co(2)-O(1)	2.0271(17)
Co(2)-O(1)#4	2.0271(17)
Co(2)-O(11)	2.0739(17)
Co(2)-O(11)#5	2.0739(17)
Co(2)-O(2)#2	2.1617(15)
Co(2)-O(2)#6	2.1617(15)
O(1)-C(1)	1.246(3)
O(11)-Co(2)#5	2.0739(17)
C(1)-C(2)#7	1.462(3)
C(1)-C(2)	1.469(3)
O(2)-C(2)	1.265(3)
O(2)-Co(2)#8	2.1617(15)
C(2)-C(1)#7	1.462(3)

O(11)-Co(1)-O(11)#1	180.0
O(11)-Co(1)-O(2)	97.55(7)
O(11)#1-Co(1)-O(2)	82.45(7)
O(11)-Co(1)-O(2)#2	82.45(7)
O(11)#1-Co(1)-O(2)#2	97.55(7)
O(2)-Co(1)-O(2)#2	93.45(9)
O(11)-Co(1)-O(2)#1	82.45(7)
O(11)#1-Co(1)-O(2)#1	97.55(7)
O(2)-Co(1)-O(2)#1	180.0
O(2)#2-Co(1)-O(2)#1	86.55(9)
O(11)-Co(1)-O(2)#3	97.55(7)
O(11)#1-Co(1)-O(2)#3	82.45(7)
O(2)-Co(1)-O(2)#3	86.55(9)
O(2)#2-Co(1)-O(2)#3	180.00(7)
O(2)#1-Co(1)-O(2)#3	93.45(9)
O(1)-Co(2)-O(1)#4	88.83(9)
O(1)-Co(2)-O(11)	95.49(7)
O(1)#4-Co(2)-O(11)	172.28(8)
O(1)-Co(2)-O(11)#5	172.28(8)
O(1)#4-Co(2)-O(11)#5	95.49(7)
O(11)-Co(2)-O(11)#5	80.96(11)
O(1)-Co(2)-O(2)#2	91.62(6)
O(1)#4-Co(2)-O(2)#2	93.46(6)
O(11)-Co(2)-O(2)#2	80.04(8)
O(11)#5-Co(2)-O(2)#2	94.50(8)
O(1)-Co(2)-O(2)#6	93.46(6)
O(1)#4-Co(2)-O(2)#6	91.62(6)
O(11)-Co(2)-O(2)#6	94.50(8)
O(11)#5-Co(2)-O(2)#6	80.05(8)
O(2)#2-Co(2)-O(2)#6	172.88(9)
C(1)-O(1)-Co(2)	132.86(16)
Co(1)-O(11)-Co(2)#5	100.97(9)
Co(1)-O(11)-Co(2)	100.97(9)
Co(2)#5-O(11)-Co(2)	99.03(11)
O(1)-C(1)-C(2)#7	133.7(2)
O(1)-C(1)-C(2)	137.2(2)
C(2)#7-C(1)-C(2)	89.07(18)
C(2)-O(2)-Co(1)	128.29(14)

C(2)-O(2)-Co(2)#8	125.33(14)
Co(1)-O(2)-Co(2)#8	95.74(6)
O(2)-C(2)-C(1)#7	133.6(2)
O(2)-C(2)-C(1)	135.4(2)
C(1)#7-C(2)-C(1)	90.93(18)

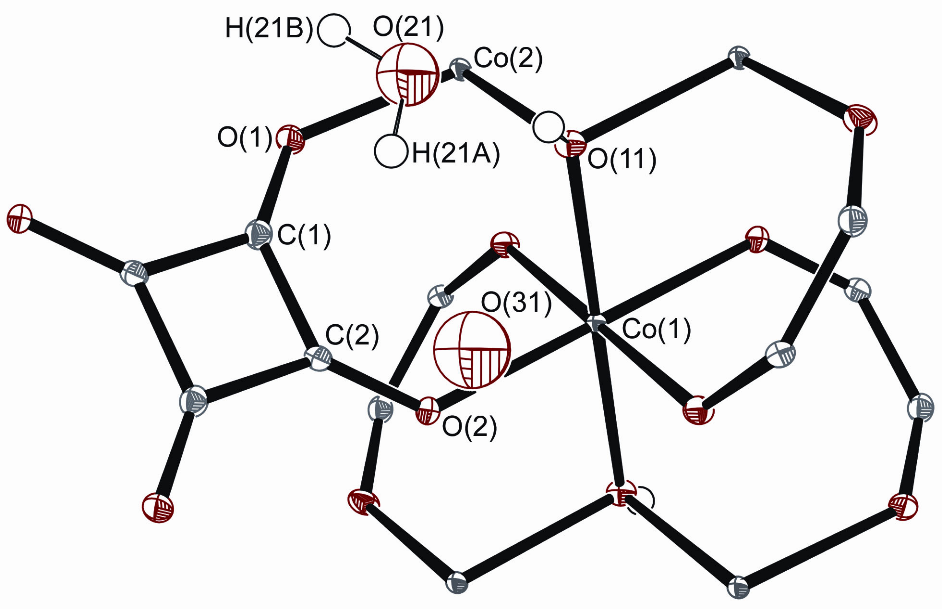
Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1   #2 -x+1,y,-z+1
#3 x,-y+1,z   #4 -x+1,y,-z   #5 -x+1,-y+1,-z
#6 x,y,z-1   #7 -x+1/2,-y+1/2,-z+1
#8 x,y,z+1

Table 10. Anisotropic displacement parameters (Å^2 x 10^4) for A at 100 K. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]

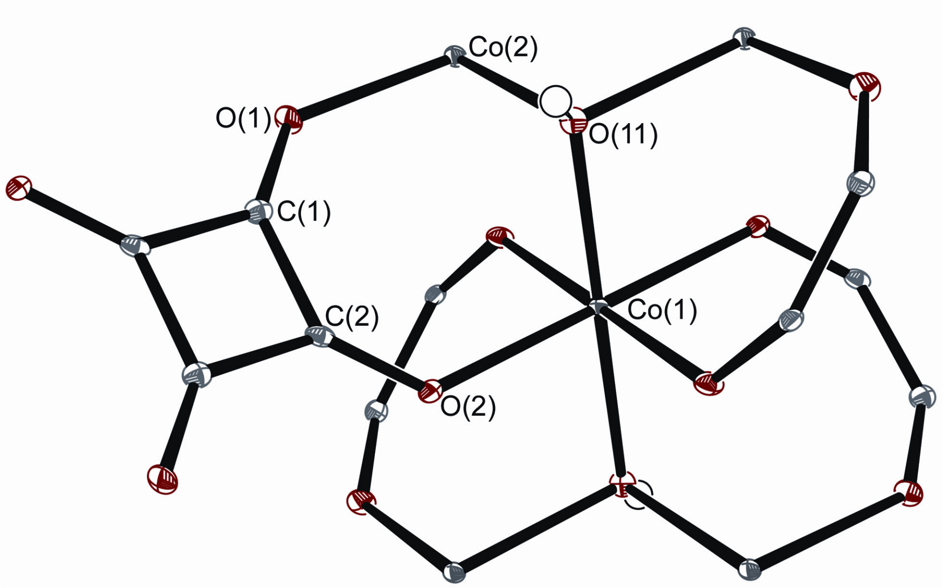
	U11	U22	U33	U23	U13	U12
Co(1)	62(3)	52(3)	33(3)	0	5(2)	0
Co(2)	65(2)	56(2)	45(2)	0	14(2)	0
O(1)	86(9)	95(8)	74(7)	5(6)	39(6)	-16(7)
O(11)	43(11)	82(11)	79(11)	0	2(9)	0
C(1)	74(11)	74(11)	69(10)	0(9)	-8(8)	15(9)
O(2)	91(9)	78(8)	55(7)	-6(6)	-5(6)	-27(6)
C(2)	79(11)	72(11)	49(10)	13(8)	4(8)	30(9)

Table 11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for A at 100 K.

	x	y	z	U(eq)
H(11)	3290(50)	5000	1580(80)	8



(a)



(b)

Fig. S4 ORTEP representation of the structures of **A·3H$_2$O** at 150 K (a) and **A** at 100 K (b) showing 50% thermal ellipsoids. The atoms of the asymmetric unit have been labelled.