Electronic Supplementary Material (ESI) for New Journal of Chemistry.

The copper sulfate hydration cycle. Crystal structures of $CuSO_4$ (Chalcocyanite), $CuSO_4 \cdot H_2O$ (Poitevinite), $CuSO_4 \cdot 3H_2O$ (Bonattite) and $CuSO_4 \cdot 5H_2O$ (Chalcanthite) at low temperature using non-spherical atomic scattering factors†

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Supplementary Information

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1. Additional notes on sample preparation and handling

Dehydration of $CuSO_4 \cdot 5H_2O$

Figure S1. A popular demonstration of dehydration. The blue pentahydrate (at left) on heating with an open flame (center) visibly loses water as steam and the core shows progressively paler blue towards the edge (right), which is commonly described as the anhydrous sulfate.

Whilst heating bulk pentahydrate with an open flame is an attractive illustration of the facile dehydration of copper(II) sulfate, this procedure is not recommended for preparation of pure anhydrous $CuSO_4$ since the temperature is difficult to control and decomposition of the sulfate ions into corrosive SO_3(g), leaving behind CuO(s) can occur. CAUTION: FUME HOOD USE IS ESSENTIAL! In many versions of the 'sequence of reactions of copper' experiments, the oxide is of course the intended product. Merely heating the pentahydrate in a laboratory oven at 120-150°C produces a gray-white solid that is thought to be primarily $CuSO_4 \cdot H_2O$. Reliable dehydration to pure $CuSO_4$ is best done by heating for several hours in a muffle furnace set to about 350 °C.[1]

Crystals of $CuSO_4 \cdot 5H_2O$ and $CuSO_4 \cdot 3H_2O$

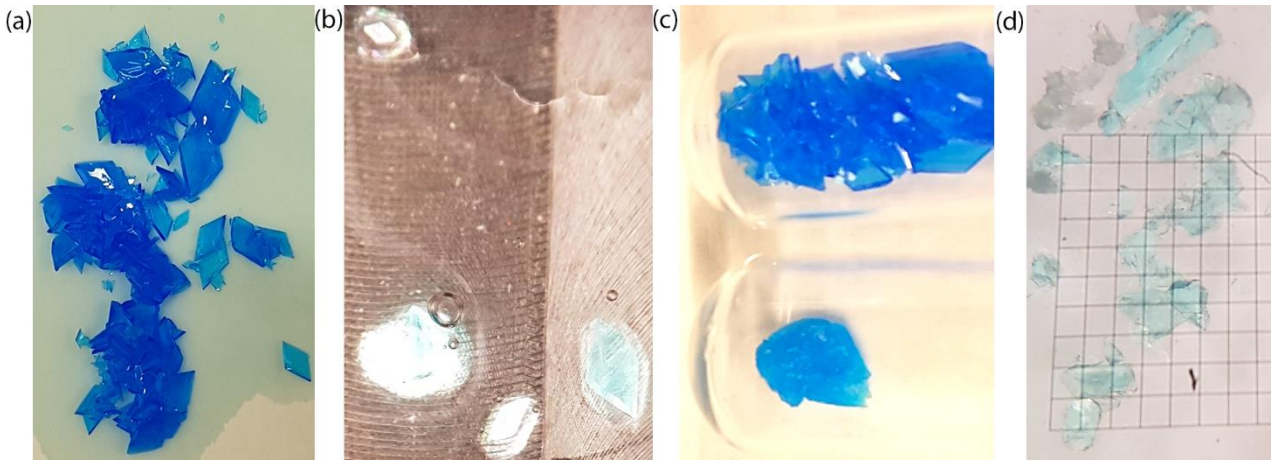

Figure S2. (a) Beautiful trapezoidal crystals of $CuSO_4 \cdot 5H_2O$ from cooling of a saturated aqueous solution and (b) the very smallest crystals from the sample viewed under the microscope. (c) The upper vial are bulk crystals of freshly grown $CuSO_4 \cdot 5H_2O$ whilst the bottom vial contains the $CuSO_4 \cdot 3H_2O$ crystals as grown. (d) Crystals of $CuSO_4 \cdot 3H_2O$ under the microscope on a white background to aid visualization.

$CuSO_4 \cdot 5H_2O$ (Fisher, technical grade) was recrystallized from a saturated aqueous solution to afford bright blue trapezoidal plates. The recrystallized material was used for all subsequent work. Several very small lozenge-shaped crystals also formed, which were used to obtain the crystal structure of **4**, after carefully

splitting these crystals multiple times to obtain a sufficiently small crystal. Buffering the crystals from shock within the Paratone® crystal mounting oil was essential to the cleaving process.

$CuSO_4 \cdot 3H_2O$ **3** was obtained using an understanding of the $CuO/SO_3/H_2O$ phase diagram [1] following the method reported by Götz.[2] 0.80 g of $CuSO_4 \cdot 5H_2O$ (8 wt.%) was dissolved in 3.7 g H_2O (37 wt.%) in a 20 mL Erlenmeyer flask and gently heated on a hot plate. To this was carefully added 5.5 g of 98% H_2SO_4 (55 wt.%) so as not to boil the solution. CAUTION: ANHYDROUS H_2SO_4 IS A STRONG DESSICANT AS WELL AS ACIDIC. PROPPER GLOVES AND EYE PROTECTION IS ESSENTIAL. ALL WORK SHOULD BE PERFORMED IN A FUME HOOD. The resulting pale blue solution was cooled slowly overnight by turning off the hot plate. In the morning, clumps of sky-blue crystals had formed, which were filtered off on a coarse fritted glass funnel, 0.27 g (34% yield). The smallest clumps were transferred to Paratone® crystal mounting oil where they presented as aggregated blocks of almost colourless crystals that could be separated with a razor blade to afford bona fide single crystals in the oil. One of these crystals was mounted on the diffractometer and identified as **3**.

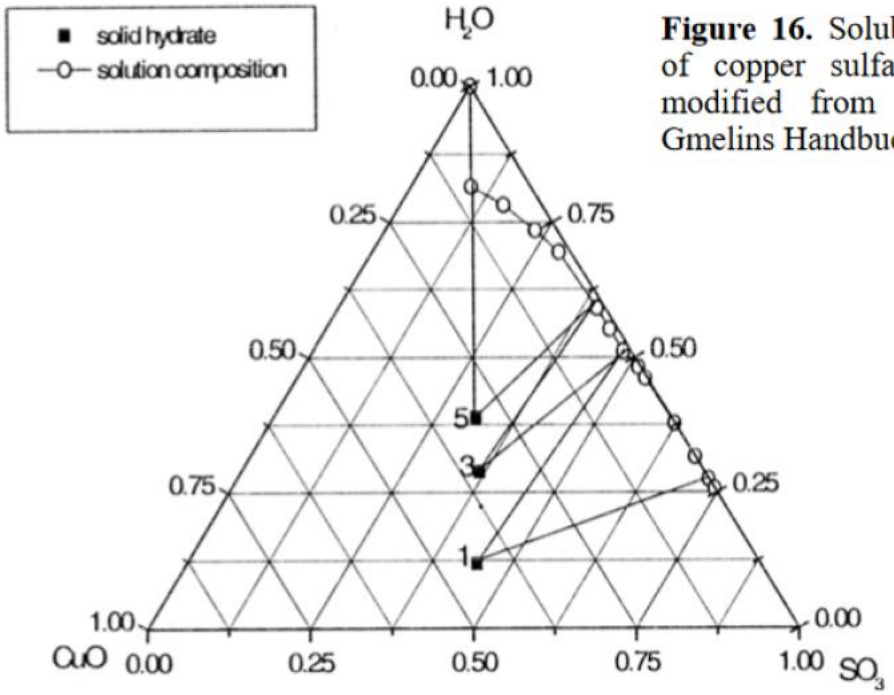

Figure 16. Solubility of the hydrates of copper sulfate in sulfuric acid; modified from Mellor (1923) and Gmelins Handbuch (1958).

Figure S3. The $CuO/SO_3/H_2O$ phase diagram presented in Ref. 1. $CuSO_4 \cdot 5H_2O$ covers a large field of stability so that the conditions for crystallization of $CuSO_4 \cdot 3H_2O$ and $CuSO_4 \cdot H_2O$ are quite restricted. (Used with permission from the Mineralogical Society of America: J. L. Jambor, D. K. Nordstrom, C. N. Alpers, *Rev. Mineral. Geochem*., 2000, **40**, 303.)

The mother liquor from the synthesis of **3** described above was gently boiled on the hot plate for 3 H and concentrated to about ¾ the original volume. On cooling overnight, clusters of palest blue crystals of **2** formed at the bottom, were filtered on the fritted funnel, transferred to a microscope slide and immersed in Paratone®. The crystals were readily identified as **2** from the unit cell parameters, but crystal quality was poor with excessively high R_{int} on intensities. Careful searching resulted in the identification of very small flat needles. These crystals were adequate but still not of excellent diffraction quality with strong evidence of some modulation. The smallest crystals, requiring the brighter Cu Kα source, gave the best results and one of these was used for the reported structure.

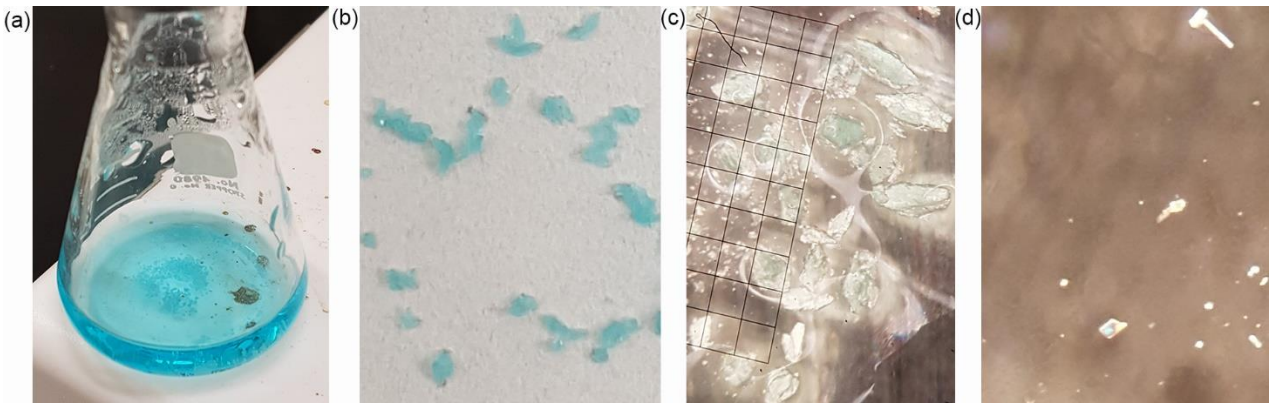

Figure S4. (a) Crystals of $CuSO_4 \cdot H_2O$ have formed after cooling the concentrated solution. (b) Crystals after filtration. (c) Bulk crystals on the microscope that diffract poorly. (d) Very small flat needles of $CuSO_4 \cdot H_2O$ such as that at top right of the image gave the best diffraction patterns.

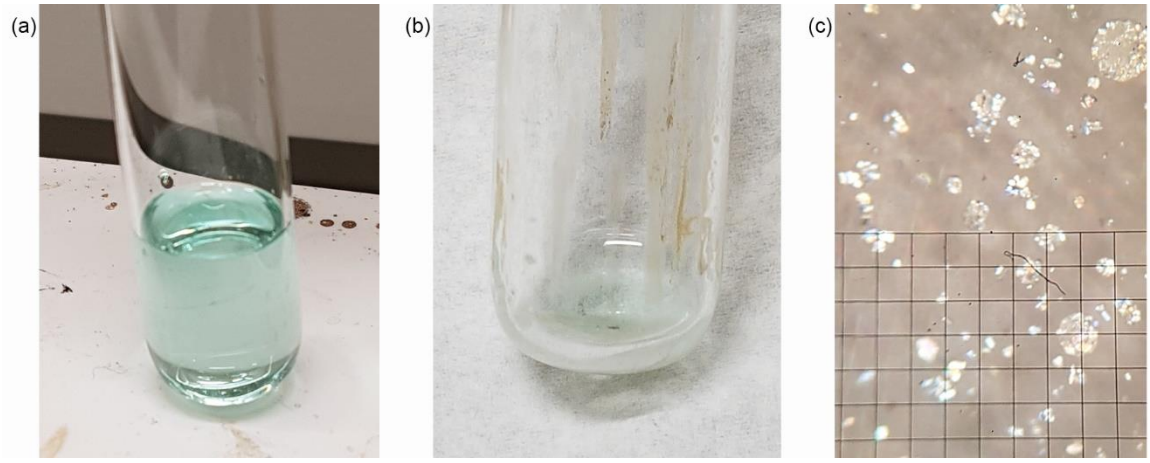

Figure S5. (a) Mother liquor for $CuSO_4$ crystal growth (20% $(NH_4)_2SO_4$/80% H_2SO_4). (b) Colourless precipitate after decanting the mother liquor. (c) Crystals of anhydrous $CuSO_4$ under the microscope.

Crystals of anhydrous $CuSO_4$ **1** were obtained following the method of Gruzensky.[3] 2.64 g $(NH_4)_2SO_4$ was dissolved by heating with an open flame in 7.84 g of 98% H_2SO_4 contained in a 20 mL borosilicate test tube and the mixture boiled for several minutes. CAUTION: ANHYDROUS H_2SO_4 IS A STRONG DESSICANT AS WELL AS ACIDIC. PROPPER GLOVES AND EYE PROTECTION IS ESSENTIAL. ALL WORK SHOULD BE PERFORMED IN A FUME HOOD. Finely ground $CuSO_4 \cdot 5H_2O$ was dehydrated in an oven at 130 °C for 3 H until grey/white in colour and added to the 20/80 mole fraction mixture until saturated at the boil. Slow cooling of the faintly blue solution was achieved by placing the end of the TT on a hot plate for several hours. Thereafter the heating was stopped, and the TT left undisturbed overnight. A fine precipitate of colourless crystals was obtained of which a portion were transferred to Paratone® crystal mounting oil. Suitable uniformly shaped prisms were selected under the microscope, mounted, and identified as **1** by the unit cell parameters. Data was collected using Mo Kα radiation at 100 K.

2. Electronic Crystal Structure Models

1. CuSO4-UnitCell.mryx
2. CuSO4-CoordinationSphere
3. CuSO4.H2O-UnitCell.mryx
4. CuSO4.H2O-CoordinationSphere
5. CuSO4.3H2O-UnitCell.mryx
6. CuSO4.3H2O-UnitCell.mryx
7. CuSO4.5H2O-CoordinationSphere
8. CuSO4.5H2O-CoordinationSphere

Eight Mercury CSD .mrxy (binary format) electronic structure model files are provided with the ESI in a ZIP archive, corresponding to the models presented in Figs. 1-5 of the paper. *Aspects of the appearance will depend on the current settings of your Mercury software, such as the Atom radii and Bond thickness, Atom colours and Label size. Whether or not H atoms are shown as displacement ellipsoids will depend on the Ellipsoid Settings… within the Display/Styles menu.*

Mercury CSD is available free of charge to the educational and research communities by the Cambridge Crystallographic Data Centre and can be downloaded from https://www.ccdc.cam.ac.uk/support-and-resources/downloads/. Mercury is of course able to read the CIF files directly, but for inorganic solids such as the copper(II) sulfates it takes some effort and advanced knowledge of the software to build the kinds of models displayed in our paper. These binary .mryx files preserve the models as built up by the authors. *This data is provided free, but explicitly without warranty or liability. Users of our provided models are responsible to learn the basics of the Mercury CSD software, which is well supported on the CCDC websites.*

3. Crystal, experimental and derived data for $CuSO_4$, 1

Table S1 Crystal data and structure refinement for CuSO4, 1.

Identification code	RB21097if
Empirical formula	CuO_4S
Formula weight	159.609
Temperature/K	100.0(3)
Crystal system	orthorhombic
Space group	*Pnma*
a/Å	8.3958(6)
b/Å	6.6760(4)
c/Å	4.8270(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	270.56(3)
Z	4
ρ_{calc}g/cm^3	3.918
μ/mm^{-1}	8.637
F(000)	310.2
Crystal size/mm^3	0.09 × 0.05 × 0.04
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	9.72 to 76.18
Index ranges	-13 ≤ h ≤ 14, -10 ≤ k ≤ 11, -7 ≤ l ≤ 8
Reflections collected	3682
Independent reflections	738 [R_{int} = 0.0344, R_{sigma} = 0.0251]
Data/restraints/parameters	738/0/34
Goodness-of-fit on F^2	1.022
Final R indexes [I>=2σ (I)]	R_1 = 0.0205, wR_2 = 0.0520
Final R indexes [all data]	R_1 = 0.0235, wR_2 = 0.0535
Largest diff. peak/hole / e Å^{-3}	0.61/-1.03

Table S2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for CuSO4, 1. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cu	0	0	0	3.64(7)
S	1837.0(5)	2500	4515.5(8)	2.40(8)
O1	1306.2(14)	2500	7388(2)	5.2(2)
O2	3642.1(14)	2500	4379(3)	4.1(2)
O3	1321.7(9)	666.9(12)	3110.5(18)	4.94(15)

Table S3 Anisotropic Displacement Parameters ($Å^2×10^3$) for CuSO4, 1. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	3.60(12)	3.05(11)	4.26(11)	0.49(6)	-1.28(6)	-0.85(6)
S	2.16(16)	2.41(15)	2.64(14)	-0	-0.13(12)	0
O1	6.0(5)	5.5(4)	4.1(5)	-0	1.4(4)	0
O2	3.1(5)	2.9(4)	6.3(5)	-0	-0.1(4)	0
O3	4.7(4)	3.8(3)	6.3(3)	-0.2(3)	-1.8(3)	-0.9(3)

Table S4 Bond Lengths for CuSO4, 1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu	$O1^1$	2.3618(8)	Cu	O3	1.9194(8)
Cu	$O1^2$	2.3618(8)	S	O1	1.4563(12)
Cu	$O2^3$	2.0433(7)	S	O2	1.5170(12)
Cu	$O2^4$	2.0433(7)	S	O3	1.4645(8)
Cu	$O3^5$	1.9194(8)	S	$O3^6$	1.4645(8)

^{1}-X,-1/2+Y,1-Z; ^{2}+X,+Y,-1+Z; ^{3}-1/2+X,1/2-Y,1/2-Z; ^{4}1/2-X,-Y,-1/2+Z; ^{5}-X,-Y,-Z; ^{6}+X,1/2-Y,+Z

Table S5 Bond Angles for CuSO4, 1.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
$O1^1$	Cu	$O1^2$	180.0	$O3^5$	Cu	O3	180.0
$O2^3$	Cu	$O1^2$	76.13(3)	O2	S	O1	110.31(7)
$O2^3$	Cu	$O1^1$	103.87(3)	O3	S	O1	110.52(4)
$O2^4$	Cu	$O1^2$	103.87(3)	$O3^6$	S	O1	110.52(4)
$O2^4$	Cu	$O1^1$	76.13(3)	$O3^6$	S	O2	105.96(4)
$O2^4$	Cu	$O2^3$	180.0	O3	S	O2	105.96(4)
O3	Cu	$O1^1$	90.84(4)	$O3^6$	S	O3	113.36(7)
O3	Cu	$O1^2$	89.16(4)	Cu^7	O1	Cu^8	89.93(4)
$O3^5$	Cu	$O1^1$	89.16(4)	S	O1	Cu^8	130.57(3)
$O3^5$	Cu	$O1^2$	90.84(4)	S	O1	Cu^7	130.57(3)
$O3^5$	Cu	$O2^3$	88.95(4)	Cu^9	O2	Cu^{10}	109.53(5)
O3	Cu	$O2^3$	91.05(4)	S	O2	Cu^{10}	123.44(3)
O3	Cu	$O2^4$	88.95(4)	S	O2	Cu^9	123.44(3)
$O3^5$	Cu	$O2^4$	91.05(4)	S	O3	Cu	136.63(5)

^{1}-X,-1/2+Y,1-Z; ^{2}+X,+Y,-1+Z; ^{3}-1/2+X,1/2-Y,1/2-Z; ^{4}1/2-X,-Y,-1/2+Z; ^{5}-X,-Y,-Z; ^{6}+X,1/2-Y,+Z; ^{7}-X,1/2+Y,1-Z; ^{8}+X,+Y,1+Z; ^{9}1/2-X,-Y,1/2+Z; ^{10}1/2+X,1/2-Y,1/2-Z

Table S6 Torsion Angles for CuSO4, 1.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
Cu[1]	O1	S	O2	-111.52(7)	Cu[5]	O2	S	O3	-41.46(9)
Cu[2]	O1	S	O2	111.52(7)	Cu[4]	O2	S	O3	162.18(7)
Cu[1]	O1	S	O3[3]	131.63(7)	Cu[5]	O2	S	O3[3]	-162.18(7)
Cu[1]	O1	S	O3	5.32(9)	Cu	O3	S	O1	119.13(8)
Cu[2]	O1	S	O3	-131.63(7)	Cu[6]	O3	S	O1	119.13(8)
Cu[2]	O1	S	O3[3]	-5.32(9)	Cu[6]	O3	S	O2	-121.37(8)
Cu[4]	O2	S	O1	-78.18(7)	Cu	O3	S	O2	-121.37(8)
Cu[5]	O2	S	O1	78.18(7)	Cu[6]	O3	S	O3[3]	-5.57(5)
Cu[4]	O2	S	O3[3]	41.46(9)	Cu	O3	S	O3[3]	-5.57(5)

[1]+X,+Y,1+Z; [2]-X,1/2+Y,1-Z; [3]+X,1/2-Y,+Z; [4]1/2+X,1/2-Y,1/2-Z; [5]1/2-X,-Y,1/2+Z; [6]-X,-Y,-Z

Refinement model description

Number of restraints - 0, number of constraints - 0.
Details:
1. Rigid body (RIGU) restrains
All non-hydrogen atoms
with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004

4. Crystal, experimental and derived data for $CuSO_4 \cdot H_2O$, 2

Table S7 Crystal data and structure refinement for $CuSO_4 \cdot H_2O$, 2.

Identification code	RB21080ai2f
Empirical formula	CuH_2O_5S
Formula weight	177.625
Temperature/K	100.01(10)
Crystal system	triclinic
Space group	P-1
a/Å	5.0281(5)
b/Å	5.1502(5)
c/Å	7.5607(9)
α/°	108.592(12)
β/°	108.382(12)
γ/°	91.359(10)
Volume/Å^3	174.41(4)
Z	2
ρ_{calc}g/cm^3	3.382
μ/mm^{-1}	13.717
F(000)	171.3
Crystal size/mm^3	0.14 × 0.06 × 0.027
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	13.14 to 160.66
Index ranges	-6 ≤ h ≤ 6, -6 ≤ k ≤ 6, -9 ≤ l ≤ 9
Reflections collected	3078
Independent reflections	751 [R_{int} = 0.0399, R_{sigma} = 0.0243]
Data/restraints/parameters	751/32/73
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0753, wR_2 = 0.2174
Final R indexes [all data]	R_1 = 0.0759, wR_2 = 0.2178
Largest diff. peak/hole / e Å^{-3}	2.49/-1.48

Table S8 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for $CuSO_4 \cdot H_2O$, 2. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cu1	5000	5000	5000	11.6(6)
Cu2	0	0	0	11.0(6)
S1	3916(4)	10745(4)	7526(3)	10.6(6)
O1	1374(14)	4397(14)	2702(9)	12.9(13)
O2	3361(14)	7703(13)	6711(10)	14.0(13)
O3	7043(13)	11635(13)	8517(10)	13.0(13)
O4	2528(14)	11710(14)	9026(10)	14.2(13)
O5	2937(14)	11969(14)	5993(10)	14.0(13)

Table S9 Anisotropic Displacement Parameters ($Å^2×10^3$) for $CuSO_4·H_2O$, 2. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu1	13.8(10)	11.7(10)	7.3(9)	1.9(7)	0.9(7)	3.0(7)
Cu2	13.7(10)	11.3(10)	6.2(9)	2.4(7)	0.6(7)	3.5(7)
S1	13.6(11)	9.2(10)	6.8(10)	1.5(7)	0.6(8)	2.4(8)
O1	15(3)	15(3)	6(3)	3(2)	1(2)	3(2)
O2	17(3)	11(3)	14(3)	3(2)	6(3)	3(3)
O3	13.3(15)	12.9(15)	12.8(14)	1.7(5)	4.3(5)	4.5(5)
O4	14.6(15)	13.9(15)	13.9(14)	1.8(5)	4.9(5)	4.5(5)
O5	14.4(15)	14.0(15)	13.6(14)	1.9(5)	4.6(5)	5.0(5)

Table S10 Bond Lengths for $CuSO_4·H_2O$, 2.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	$O1^1$	2.018(6)	Cu2	$O3^1$	1.946(6)
Cu1	O1	2.018(6)	Cu2	$O3^5$	1.946(6)
Cu1	O2	1.967(6)	Cu2	$O4^6$	1.971(6)
Cu1	$O2^1$	1.967(6)	Cu2	$O4^7$	1.971(6)
Cu1	$O5^2$	2.289(6)	S1	O2	1.472(7)
Cu1	$O5^3$	2.289(6)	S1	O3	1.499(7)
Cu2	$O1^4$	2.422(7)	S1	O4	1.476(7)
Cu2	O1	2.422(7)	S1	O5	1.450(7)

[1]1-X,1-Y,1-Z; [2]1-X,2-Y,1-Z; [3]+X,-1+Y,+Z; [4]-X,-Y,-Z; [5]-1+X,-1+Y,-1+Z; [6]-X,1-Y,1-Z; [7]+X,-1+Y,-1+Z

Table S11 Bond Angles for $CuSO_4·H_2O$, 2.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
$O1^1$	Cu1	O1	180.0	$O4^6$	Cu2	O1	83.0(2)
O2	Cu1	O1	89.0(3)	$O4^6$	Cu2	$O1^4$	97.0(2)
O2	Cu1	$O1^1$	91.0(3)	$O4^7$	Cu2	O1	97.0(2)
$O2^1$	Cu1	O1	91.0(3)	$O4^7$	Cu2	$O1^4$	83.0(2)
$O2^1$	Cu1	$O1^1$	89.0(3)	$O4^6$	Cu2	$O3^5$	85.5(3)
$O2^1$	Cu1	O2	180.0	$O4^7$	Cu2	$O3^1$	85.5(3)
$O5^2$	Cu1	O1	89.1(2)	$O4^6$	Cu2	$O3^1$	94.5(3)
$O5^3$	Cu1	$O1^1$	89.1(2)	$O4^7$	Cu2	$O3^5$	94.5(3)
$O5^3$	Cu1	O1	90.9(2)	$O4^7$	Cu2	$O4^6$	180.0
$O5^2$	Cu1	$O1^1$	90.9(2)	O3	S1	O2	109.1(4)
$O5^2$	Cu1	O2	82.5(3)	O4	S1	O2	108.2(4)
$O5^3$	Cu1	$O2^1$	82.5(3)	O4	S1	O3	108.8(4)
$O5^3$	Cu1	O2	97.5(3)	O5	S1	O2	112.1(4)
$O5^2$	Cu1	$O2^1$	97.5(3)	O5	S1	O3	107.8(4)
$O5^3$	Cu1	$O5^2$	180.0	O5	S1	O4	110.9(4)
$O1^4$	Cu2	O1	180.0	Cu2	O1	Cu1	119.4(3)
$O3^1$	Cu2	O1	91.4(2)	S1	O2	Cu1	130.9(4)
$O3^1$	Cu2	$O1^4$	88.6(2)	S1	O3	$Cu2^1$	131.6(4)
$O3^5$	Cu2	O1	88.6(2)	S1	O4	$Cu2^8$	136.3(4)
$O3^5$	Cu2	$O1^4$	91.4(2)	S1	O5	$Cu1^9$	134.7(4)
$O3^1$	Cu2	$O3^5$	180.0				

[1]1-X,1-Y,1-Z; [2]+X,-1+Y,+Z; [3]1-X,2-Y,1-Z; [4]-X,-Y,-Z; [5]-1+X,-1+Y,-1+Z; [6]+X,-1+Y,-1+Z; [7]-X,1-Y,1-Z; [8]+X,1+Y,1+Z; [9]+X,1+Y,+Z

Table S12 Hydrogen Bonds for $CuSO_4 \cdot H_2O$, 2.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O1	H1a	O3[1]	0.992(19)	1.70(3)	2.692(9)	173(14)
O1	H1b	O2[2]	0.992(19)	1.91(9)	2.808(9)	150(14)
O1	H1b	O5[3]	0.992(19)	2.38(13)	3.088(9)	128(12)

[1]1-X,2-Y,1-Z; [2]-X,1-Y,1-Z; [3]-X,2-Y,1-Z

Table S13 Torsion Angles for $CuSO_4 \cdot H_2O$, 2.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
Cu1	O2	S1	O3	-50.9(6)	Cu2[4]	O3	S1	O2	-34.5(6)
Cu1[1]	O2	S1	O3	-50.9(6)	Cu2[1]	O3	S1	O2	-34.5(6)
Cu1	O2	S1	O4	-169.0(5)	Cu2[4]	O3	S1	O4	83.2(6)
Cu1[1]	O2	S1	O4	-169.0(5)	Cu2[1]	O3	S1	O4	83.2(6)
Cu1	O2	S1	O5	68.4(6)	Cu2[4]	O3	S1	O5	-156.4(5)
Cu1[1]	O2	S1	O5	68.4(6)	Cu2[1]	O3	S1	O5	-156.4(5)
Cu1[2]	O5	S1	O2	-124.8(5)	Cu2[5]	O4	S1	O2	-5.6(7)
Cu1[3]	O5	S1	O2	-124.8(5)	Cu2[6]	O4	S1	O2	-5.6(7)
Cu1[2]	O5	S1	O3	-4.8(6)	Cu2[6]	O4	S1	O3	-123.9(6)
Cu1[3]	O5	S1	O3	-4.8(6)	Cu2[5]	O4	S1	O3	-123.9(6)
Cu1[2]	O5	S1	O4	114.2(6)	Cu2[6]	O4	S1	O5	117.8(6)
Cu1[3]	O5	S1	O4	114.2(6)	Cu2[5]	O4	S1	O5	117.8(6)

[1]1-X,1-Y,1-Z; [2]+X,1+Y,+Z; [3]1-X,2-Y,1-Z; [4]1+X,1+Y,1+Z; [5]+X,1+Y,1+Z; [6]-X,1-Y,1-Z

Table S14 Hydrogen Atom Coordinates (Å×10[4]) and Isotropic Displacement Parameters (Å[2]×10[3]) for $CuSO_4 \cdot H_2O$, 2.

Atom	*x*	*y*	*z*	U(eq)
H1a	2100(300)	5800(200)	2300(200)	15.5(16)
H1b	-450(180)	4300(300)	2900(200)	15.5(16)

Refinement model description

Number of restraints - 8, number of constraints - 2.
Details:
1. Fixed Uiso
 At 1.2 times of:
  All O(H,H) groups
2. Restrained distances
 O1-H1a = O1-H1b
 0.989 with sigma of 0.02
3. Uiso/Uaniso restraints and constraints
Uanis(O1) ≈ Ueq, Uanis(O2) ≈ Ueq, Uanis(O5) ≈ Ueq, Uanis(O3) ≈
Ueq, Uanis(O4) ≈ Ueq: with sigma of 0.05 and sigma for terminal atoms of
0.001
4. Rigid body (RIGU) restrains
 S1, Cu2, Cu1
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004

5. Crystal, experimental and derived data for $CuSO_4 \cdot 3H_2O$, 3

Table S15 Crystal data and structure refinement for $CuSO_4 \cdot 3H_2O$, 3.

Identification code	RB21092_auto
Empirical formula	CuH_6O_7S
Formula weight	213.655
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	Cc
a/Å	5.5708(2)
b/Å	12.9751(4)
c/Å	7.3754(2)
α/°	90
β/°	96.450(3)
γ/°	90
Volume/Å^3	529.73(3)
Z	4
ρ_{calc}g/cm^3	2.679
μ/mm^{-1}	4.488
F(000)	430.3
Crystal size/mm^3	0.101 × 0.07 × 0.057
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.28 to 76.32
Index ranges	-9 ≤ h ≤ 9, -22 ≤ k ≤ 21, -12 ≤ l ≤ 12
Reflections collected	13522
Independent reflections	2761 [R_{int} = 0.0375, R_{sigma} = 0.0284]
Data/restraints/parameters	2761/128/136
Goodness-of-fit on F^2	1.012
Final R indexes [I>=2σ (I)]	R_1 = 0.0188, wR_2 = 0.0424
Final R indexes [all data]	R_1 = 0.0194, wR_2 = 0.0429
Largest diff. peak/hole / e Å^{-3}	0.39/-0.81
Flack parameter	0.001(4)

Table S16 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for $CuSO_4 \cdot 3H_2O$, 3. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cu1	4126.6(2)	6350.78(10)	3506.72(18)	4.53(3)
O1	5735.4(17)	6649.9(8)	5947.2(12)	7.28(16)
O2	8911.4(16)	5543.8(8)	7319.4(13)	9.08(16)
O3	4938.2(16)	5439.3(7)	8329.3(13)	8.07(15)
O4	7380.5(17)	6957.9(8)	9010.0(12)	7.74(15)
O5	6995.4(16)	6943.2(8)	2605.1(12)	7.90(15)
O6	2462.9(19)	6286.0(7)	989.4(15)	7.58(17)
O7	1063.0(16)	5905.3(8)	4330.1(12)	6.98(15)
S1	6750.1(5)	6129.7(2)	7672.3(4)	3.84(5)

Table S17 Anisotropic Displacement Parameters ($Å^2×10^3$) for $CuSO_4·3H_2O$, 3. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu1	4.04(5)	6.13(6)	3.44(5)	-0.82(5)	0.50(4)	0.03(5)
O1	8.8(4)	7.7(4)	5.0(4)	0.8(3)	-1.0(3)	0.7(3)
O2	7.9(3)	10.8(4)	9.1(4)	4.9(3)	3.6(3)	3.2(3)
O3	9.0(3)	6.6(3)	9.1(4)	-2.2(3)	3.4(3)	0.1(3)
O4	10.7(4)	7.1(4)	5.2(3)	-1.9(3)	0.2(3)	-1.5(3)
O5	6.6(3)	10.0(4)	7.4(4)	-0.7(3)	2.1(3)	0.8(3)
H5a	12(9)	46(18)	11(4)	-2(6)	2.6(19)	1(2)
H5b	7(5)	15(13)	15(7)	0(3)	0(2)	0(5)
O6	7.8(4)	9.5(4)	5.4(4)	-0.1(3)	0.4(3)	-0.0(3)
H6a	11(8)	23(10)	5(5)	5(4)	-2(3)	0(3)
H6b	14(11)	18(6)	22(9)	6(4)	1(4)	5(3)
O7	6.8(3)	7.8(4)	6.5(3)	-1.2(3)	1.5(3)	-0.2(3)
H7a	13(10)	11(7)	15(8)	-3(4)	3(4)	-2(4)
H7b	34(11)	26(11)	13(4)	-12(5)	11(2)	-4(2)
S1	4.19(10)	4.0(1)	3.38(10)	0.05(8)	0.65(8)	0.05(8)

Table S18 Bond Lengths for $CuSO_4·3H_2O$, 3.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	O1	1.9574(9)	O1	S1	1.4941(10)
Cu1	$O3^1$	2.3726(10)	O2	S1	1.4717(10)
Cu1	O5	1.9560(9)	O3	S1	1.4717(10)
Cu1	O6	1.9816(11)	O4	S1	1.4743(10)
Cu1	O7	1.9618(9)	Cu1	O4	2.4460(10)

^{1}+X,1-Y,-1/2+Z

Table S19 Bond Angles for $CuSO_4·3H_2O$, 3.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
$O3^1$	Cu1	O1	100.05(4)	O7	Cu1	O6	86.90(4)
O5	Cu1	O1	85.84(4)	S1	O1	Cu1	141.61(7)
O5	Cu1	$O3^1$	101.41(4)	S1	O3	$Cu1^2$	139.11(6)
O6	Cu1	O1	170.99(4)	O2	S1	O1	108.76(6)
O6	Cu1	$O3^1$	88.78(4)	O3	S1	O1	110.34(6)
O6	Cu1	O5	90.70(4)	O3	S1	O2	110.41(6)
O7	Cu1	O1	95.63(4)	O4	S1	O1	106.23(6)
O7	Cu1	$O3^1$	84.63(4)	O4	S1	O2	110.90(6)
O7	Cu1	O5	173.46(4)	O4	S1	O3	110.12(6)

^{1}+X,1-Y,-1/2+Z; ^{2}+X,1-Y,1/2+Z

Table S20 Hydrogen Bonds for $CuSO_4 \cdot 3H_2O$, 3.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O5	H5a	O4[1]	0.998(15)	1.687(16)	2.6841(13)	178(3)
O5	H5b	O7[2]	1.001(15)	1.890(19)	2.8141(13)	152(2)
O6	H6a	O3[1]	0.978(15)	1.776(16)	2.7505(14)	174(2)
O6	H6b	O1[3]	0.993(16)	1.94(2)	2.8448(15)	151(2)
O6	H6b	O4[4]	0.993(16)	2.48(2)	3.1589(15)	125(2)
O7	H7a	O2[5]	1.000(15)	1.621(16)	2.6022(13)	166(2)
O7	H7b	O2[6]	0.954(16)	1.78(2)	2.6667(13)	153(3)

[1]+X,+Y,-1+Z; [2]1+X,+Y,+Z; [3]-1/2+X,3/2-Y,-1/2+Z; [4]-1+X,+Y,-1+Z; [5]-1+X,1-Y,-1/2+Z; [6]-1+X,+Y,+Z

Table S21 Torsion Angles for $CuSO_4 \cdot 3H_2O$, 3.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
Cu1	O1	S1	O2	68.25(11)	Cu1[1]	O3	S1	O1	106.11(9)
Cu1	O1	S1	O3	-53.00(11)	Cu1[1]	O3	S1	O2	-14.15(10)
Cu1	O1	S1	O4	-172.33(10)	Cu1[1]	O3	S1	O4	-136.94(8)

[1]+X,1-Y,1/2+Z

Table S22 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for $CuSO_4 \cdot 3H_2O$, 3.

Atom	*x*	*y*	*z*	U(eq)
H5a	7120(50)	6930(30)	1270(20)	23(6)
H5b	8500(30)	6790(20)	3430(30)	12(5)
H6a	3360(40)	6030(20)	20(30)	13(5)
H6b	1560(50)	6920(16)	590(40)	18(5)
H7a	400(40)	5273(15)	3680(30)	13(5)
H7b	720(60)	5880(20)	5570(20)	24(5)

Refinement model description

Number of restraints - 128, number of constraints - 0.
Details:
1. Restrained distances
O6-H6b = O6-H6a = O5-H5a = O5-H5b = O7-H7b = O7-H7a
0.989 with sigma of 0.02
2. Uiso/Uaniso restraints and constraints
Uanis(H7b) ≈ Ueq, Uanis(H6a) ≈ Ueq: with sigma of 0.01 and sigma for terminal atoms of 0.02
3. Rigid body (RIGU) restrains
Cu1, O1, O1, O1, O2, O2, O2, O3, O3, O3, O4, O4, O4, O5, H5a, H5b, O6, H6a, H6b, O7, H7a, H7b, S1, S1, S1
with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
H7b, H6b, H5b, H5a
with sigma for 1-2 distances of 0.001 and sigma for 1-3 distances of 0.001

5. Crystal, experimental and derived data for $CuSO_4 \cdot 5H_2O$, 4

Table S23 Crystal data and structure refinement for $CuSO_4 \cdot 5H_2O$, 4.

Identification code	RB21086i
Empirical formula	$CuH_{10}O_9S$
Formula weight	249.686
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	5.9676(2)
b/Å	6.0957(2)
c/Å	10.6366(3)
α/°	77.224(3)
β/°	82.387(2)
γ/°	72.434(3)
Volume/Å^3	358.85(2)
Z	2
ρ_{calc}g/cm^3	2.311
μ/mm^{-1}	3.350
F(000)	255.2
Crystal size/mm^3	0.222 × 0.173 × 0.135
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	7.14 to 76.6
Index ranges	-10 ≤ h ≤ 10, -10 ≤ k ≤ 10, -17 ≤ l ≤ 18
Reflections collected	18712
Independent reflections	3729 [R_{int} = 0.0463, R_{sigma} = 0.0349]
Data/restraints/parameters	3729/70/193
Goodness-of-fit on F^2	1.076
Final R indexes [I>=2σ (I)]	R_1 = 0.0249, wR_2 = 0.0494
Final R indexes [all data]	R_1 = 0.0290, wR_2 = 0.0513
Largest diff. peak/hole / e Å^{-3}	0.56/-0.63

Table S24 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for $CuSO_4 \cdot 5H_2O$, 4. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cu1	5000	5000	5000	5.32(4)
S1	8739.4(4)	5141.7(4)	2142.9(2)	4.58(4)
O1	3510.3(14)	3149.7(13)	4255.9(7)	8.92(13)
Cu2	5000	10000	0	5.07(4)
O2	6529.8(13)	2087.5(13)	6181.7(7)	8.62(13)
O3	7972.9(14)	10343.1(14)	-952.3(8)	12.10(15)
O4	5200.5(14)	7412.1(14)	-826.9(8)	13.19(15)
O6	8253.3(13)	4049.0(13)	3494.0(7)	8.21(13)
O7	8623.8(13)	3628.9(13)	1259.0(7)	8.64(13)
O8	11157.9(12)	5434.0(13)	1999.8(7)	7.53(12)
O9	7030.3(13)	7481.0(12)	1833.6(7)	8.52(13)
O5	1312.5(14)	663.8(13)	6250.9(8)	9.82(13)

Table S25 Anisotropic Displacement Parameters (Å^2×10^3) for $CuSO_4 \cdot 5H_2O$, 4. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu1	5.53(7)	5.20(7)	5.53(7)	-1.73(5)	-0.63(5)	-1.23(5)
S1	4.37(9)	4.18(9)	5.22(9)	-1.19(7)	0.30(7)	-1.37(7)
O1	9.9(3)	9.5(3)	8.9(3)	-4.5(3)	-1.5(3)	-1.8(2)
H1a	24(8)	27(8)	24(8)	-6(4)	-1(4)	-9(4)
H1b	20(8)	18(8)	25(8)	-8(4)	5(4)	-3(4)
Cu2	4.87(7)	4.74(7)	6.26(7)	-2.19(5)	1.39(5)	-2.29(5)
O2	9.0(3)	8.3(3)	8.0(3)	-2.2(3)	-0.8(2)	-0.5(2)
H2a	20(6)	19(6)	19(6)	-6(2)	1(2)	-3(2)
H2b	23(6)	20(6)	15(6)	-6(2)	-1(2)	-4(2)
O3	8.2(3)	8.0(3)	18.3(4)	-2.3(3)	4.9(3)	-2.3(3)
H3a	33(8)	26(8)	16(8)	-12(4)	-1(4)	-9(4)
H3b	30(9)	25(8)	26(8)	-5(4)	-3(4)	-8(4)
O4	7.4(3)	12.5(4)	23.3(4)	-2.7(3)	0.9(3)	-12.3(3)
H4a	32(8)	27(8)	27(9)	-8(4)	-4(4)	-2(4)
H4b	26(8)	27(8)	34(9)	-10(4)	-2(4)	-4(4)
O6	9.7(3)	6.8(3)	7.0(3)	-2.2(2)	1.3(2)	-0.3(2)
O7	7.9(3)	9.2(3)	10.4(3)	-2.2(2)	-1.1(2)	-5.2(2)
O8	6.1(3)	8.1(3)	9.5(3)	-3.2(2)	0.4(2)	-2.8(2)
O9	8.8(3)	6.3(3)	7.9(3)	1.1(2)	-0.5(2)	-0.8(2)
O5	10.1(3)	7.5(3)	11.7(3)	-2.3(3)	0.1(3)	-2.3(3)
H5a	42(10)	45(9)	38(9)	-12(5)	-1(5)	-7(5)
H5b	34(9)	28(9)	36(9)	-16(4)	-3(5)	-6(4)

Table S26 Bond Lengths for $CuSO_4 \cdot 5H_2O$, 4.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	O1	1.9686(8)	S1	O8	1.4910(7)
Cu1	O1[1]	1.9686(8)	S1	O9	1.4783(7)
Cu1	O2	1.9759(7)	Cu2	O3[2]	1.9676(7)
Cu1	O2[1]	1.9759(7)	Cu2	O3	1.9676(7)
Cu1	O6[1]	2.3619(7)	Cu2	O4	1.9360(8)
Cu1	O6	2.3619(7)	Cu2	O4[2]	1.9360(8)
S1	O6	1.4751(7)	Cu2	O9[2]	2.4100(7)
S1	O7	1.4758(8)	Cu2	O9	2.4100(7)

[1]1-X,1-Y,1-Z; [2]1-X,2-Y,-Z

Table S27 Bond Angles for $CuSO_4 \cdot 5H_2O$, 4.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
O1[1]	Cu1	O1	180.0	O9	S1	O7	110.96(4)
O2	Cu1	O1	88.30(3)	O9	S1	O8	108.65(4)
O2[1]	Cu1	O1	91.70(3)	O3[2]	Cu2	O3	180.0
O2[1]	Cu1	O1[1]	88.30(3)	O4	Cu2	O3[2]	90.39(3)
O2	Cu1	O1[1]	91.70(3)	O4[2]	Cu2	O3	90.39(3)
O2	Cu1	O2[1]	180.0	O4	Cu2	O3	89.61(3)
O6[1]	Cu1	O1[1]	87.82(3)	O4[2]	Cu2	O3[2]	89.61(3)
O6[1]	Cu1	O1	92.18(3)	O4	Cu2	O4[2]	180.0
O6	Cu1	O1[1]	92.18(3)	O9[2]	Cu2	O3[2]	91.97(3)
O6	Cu1	O1	87.82(3)	O9	Cu2	O3	91.97(3)
O6	Cu1	O2[1]	92.28(3)	O9	Cu2	O3[2]	88.03(3)
O6[1]	Cu1	O2[1]	87.72(3)	O9[2]	Cu2	O3	88.03(3)
O6[1]	Cu1	O2	92.28(3)	O9[2]	Cu2	O4	86.65(3)
O6	Cu1	O2	87.72(3)	O9	Cu2	O4	93.35(3)
O6	Cu1	O6[1]	180.0	O9[2]	Cu2	O4[2]	93.35(3)
O7	S1	O6	110.26(4)	O9	Cu2	O4[2]	86.65(3)
O8	S1	O6	108.62(4)	O9[2]	Cu2	O9	180.0
O8	S1	O7	108.84(4)	S1	O6	Cu1[1]	132.10(4)
O9	S1	O6	109.46(4)	Cu2	O9	S1	138.36(4)

[1]1-X,1-Y,1-Z; [2]1-X,2-Y,-Z

Table S28 Torsion Angles for $CuSO_4 \cdot 5H_2O$, 4.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
Cu1[1]	O6	S1	O7	-108.98(6)	Cu1	O6	S1	O8	131.84(6)
Cu1	O6	S1	O7	-108.98(6)	Cu1[1]	O6	S1	O9	13.35(7)
Cu1[1]	O6	S1	O8	131.84(6)	Cu1	O6	S1	O9	13.35(7)

[1]1-X,1-Y,1-Z

Table S29 Hydrogen Bonds for $CuSO_4 \cdot 5H_2O$, 4.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O1	H1a	O6[1]	0.962(14)	2.494(17)	3.1997(11)	130.1(14)
O1	H1a	O8[1]	0.962(14)	1.875(15)	2.8113(11)	163.5(17)
O1	H1b	O5	0.950(13)	1.812(14)	2.7494(11)	168.4(18)
O2	H2a	O3[2]	0.971(14)	2.517(18)	3.1423(11)	122.1(14)
O2	H2a	O9[3]	0.971(14)	1.895(16)	2.7855(10)	151.3(17)
O2	H2b	O5[4]	0.947(13)	1.781(13)	2.7271(11)	176.2(17)
O3	H3a	O7[5]	0.964(14)	1.754(14)	2.7017(11)	166.7(17)
O3	H3b	O8[6]	0.969(14)	1.791(14)	2.7424(11)	166.5(18)
O4	H4a	O7[7]	0.947(14)	1.720(15)	2.6653(11)	175.7(19)
O4	H4b	O8[5]	0.961(14)	1.752(15)	2.6930(10)	166(2)
O5	H5a	O6[8]	0.964(15)	1.810(15)	2.7601(11)	167.6(19)
O5	H5b	O9[3]	0.963(15)	2.015(16)	2.9388(11)	160.0(19)

[1]-1+X,+Y,+Z; [2]+X,-1+Y,1+Z; [3]1-X,1-Y,1-Z; [4]1+X,+Y,+Z; [5]2-X,1-Y,-Z; [6]2-X,2-Y,-Z; [7]1-X,1-Y,-Z; [8]1-X,-Y,1-Z

Table S30 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for $CuSO_4 \cdot 5H_2O$, 4.

Atom	*x*	*y*	*z*	U(eq)
H1a	2440(30)	3950(30)	3592(16)	25(5)
H1b	2690(30)	2210(30)	4859(17)	21(5)
H2a	5740(30)	1980(30)	7042(15)	19(5)
H2b	8180(20)	1610(30)	6241(17)	19(4)
H3a	9350(30)	9050(30)	-1040(18)	24(5)
H3b	8450(30)	11770(30)	-1221(18)	27(5)
H4a	3890(30)	6970(30)	-984(19)	29(5)
H4b	6660(30)	6480(30)	-1170(20)	29(5)
H5a	1690(40)	-1000(30)	6280(20)	42(6)
H5b	2030(40)	890(40)	6955(17)	31(6)

Refinement model description

Number of restraints - 70, number of constraints - 0.
Details:
1. Restrained distances
O5-H5a = O5-H5b = O2-H2a = O2-H2b = O1-H1b = O1-H1a = O4-H4a = O4-H4b = O3-H3b = O3-H3a
0.989 with sigma of 0.02
2. Uiso/Uaniso restraints and constraints
Uanis(H1a) ≈ Ueq, Uanis(H1b) ≈ Ueq, Uanis(H3a) ≈ Ueq, Uanis(H3b) ≈ Ueq, Uanis(H4a) ≈ Ueq, Uanis(H4b) ≈ Ueq, Uanis(H5a) ≈ Ueq, Uanis(H5b) ≈ Ueq: with sigma of 0.01 and sigma for terminal atoms of 0.01
Uanis(H2a) ≈ Ueq, Uanis(H2b) ≈ Ueq: with sigma of 0.005 and sigma for terminal atoms of 0.005
3. Rigid body (RIGU) restrains
All non-hydrogen atoms
with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004

6. References for the Supporting Information

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3. P. M. Gruzensky, *J. Res. Nat'l. Bur. Stand. A. Phys. Chem.*, 1964, **54**A, 313-315.