S1. Supplementary Material

S1.1. Supplementary tables

Table S1. Crystal data and refinement

Compound	1	2a	2b
Empirical formula	$C_{10}H_{16.07}CuN_3O_{5.54}$	$C_{10}H_{24}CuN_2O_8$	$C_{20}H_{43}Cu_3N_4O_{14}$
Formula weight M[g mol^{-1}]	330.51	363.85	754.20
Crystal dimension[mm^3]	0.5 × 0.07 × 0.07	0.1 × 0.08 × 0.06	0.3 × 0.12 × 0.08
Wavelength/Å	0.71073	0.61992	0.71073
Crystal shape	rod	block	rod
Crystal color	blue	blue	blue
Crystal system	orthorhombic	monoclinic	monoclinic
Space group (no.)	$P2_12_12$ (18)	$P2_1$(4)	$P2_1/n$ (14)
T[K]	100(2)	100(2)	100(2)
a[Å]	18.897(3)	6.671(3)	7.549(5)
b[Å]	6.7444(10)	15.128(7)	14.006(10)
c[Å]	10.3301(16)	7.776(4)	13.509(10)
β[°]		90.300(8)	90.198(15)
V[Å]^3	1316.6(3)	784.7(6)	1428.3(18)
Z	4	2	2
μ[mm^{-1}]	1.684	1.013	2.286
F(000)	682	382	780
Scan range (θ)[°]	2.0 / 29.7	1.2 / 36.0	1.5/ 30.7
Reflections (total/unique)	18667 / 3542	26764 / 9016	22157/ 4292
Variables refined	186	214	219
R_{int}	0.0862	0.0557	0.1784
wR_2(all/obs.)	0.1363 / 0.130	0.1563 / 0.1428	0.1645/ 0.1409
R_1(all/obs.)	0.0782 / 0.0552	0.0675 / 0.0596	0.1100/ 0.0682
GOF on F^2	1.051	1.044	0.997
Diff. Peak/hole [e/Å]	1.622 and –0.628	2.140 and –3.808	0.828 and –1.039
Compound	**2c**	**3a**	
Empirical formula	$C_{10}H_{24}CuN_2O_8$	$C_{22}H_{25}CuO_{11}$	
Formula weight M[g mol^{-1}]	363.85	528.96	
Crystal dimension[mm^3]	0.1 × 0.09 × 0.08	0.4 × 0.07 × 0.03	
Wavelength/Å	0.61992	0.61992	
Crystal shape	block	needle	
Crystal color	blue	colorless	
Crystal system	orthorhombic	monoclinic	
Space group (no.)	*Pccn* (56)	$P2_1$(4)	
T[K]	100(2)	100(2)	
a[Å]	6.642(5)	9.070(3)	
b[Å]	15.032(10)	10.990(3)	
c[Å]	15.151(10)	12.080(3)	
β[°]		90.000(15)	
V[Å]^3	1512.7(19)	1204.1(6)	
Z	4	2	
μ[mm]$^{-1}$	1.024	0.667	
F(000)	764	548	
Scan range (θ)[°]	2.3 / 35.8	1.5 / 36.9	
Reflections (total/unique)	49974/4932	41532/15416	
Variables refined	105	323	
R_{int}	0.0506	0.0531	
wR_2(all/obs.)	0.1311/ 0.1298	0.1703 / 0.1516	
R_1(all/obs.)	0.0547/ 0.0522	0.0880/0.606	
GOF on F^2	1.118	1.029	
Diff. Peak/hole [e/Å]	1.267 and –1.376	1.312 and –2.149	

Table S2. Bond length and U_{iso}(H) for carbon bonded Hydrogen.

	C–H	$\mathbf{U_{iso}}$**(H)**
Hydroxy group	1.0 Å	1.2 × U_{eq}(C)
Methyl group	0.98 Å	1.5 × U_{eq}(C)
sp^2 hybridisation	0.95 Å	1.2 × U_{eq}(C)
sp^3 hybridisation	0.99 Å	1.2 × U_{eq}(C)

Table S3. Selected geometric parameters (Å,°) for **1**.

Cu1 – N1	1.989(5)	N1 – Cu1 – O5	90.5(2)
Cu1 – O1	1.991(4)	O1 – Cu1 – N3	82.17(19)
Cu1 – N2	1.992(5)	O1 – Cu1 – N2	173.2(2)
Cu1 – N3	2.010(5)	O1 – Cu1 – O5	94.62(17)
Cu1 – N5	2.374(5)	N3 – Cu1 – N2	102.4(2)
		O5 – Cu1 – N3	91.57(18)
N1 – Cu1 – O1	92.5(2)	O5 – Cu1 – N2	90.22 (18)
N1 – Cu1 – N3	174.4(2)		
N1 – Cu1 – N2	82.6(2)		

Table S4. Selected geometric parameters (Å, °) for **2a**.

Cu1 – O1	1.967(4)	O1 – Cu1 – O4″	84.63(14)
Cu1 – O6″	1.990(4)	O6″ – Cu1 – N1	90.16(18)
Cu1 – N1	2.052(5)	O6″ – Cu1 – N1	170.90(15)
Cu1 – N2	2.072(4)	O6″ - Cu1 – N1	86.35(14)
Cu1 – O3	2.363(4)	O6″ - Cu1 – O4″	75.11(14)
Cu1 – O4″	2.388(4)	N1 – Cu1 – N2	85.97(19)
		N1 – Cu1 – O3	97.77(16)
O1 – Cu1 - O6″	95.42(17)	N1 – Cu1 – O4″	103.40(15)
O1 – Cu1 - N1	171.21(16)	N2 – Cu1 – O3	102.32(16)
O1 – Cu1 - N2	89.44(19)	N2 – Cu1 – O4″	97.77(15)
O1 – Cu1 - O3	75.88(14)	O3 – Cu1 – O4″	151.68(11)

′ = x-1, y, z; ″= x+1, y, z

Table S5. Selected geometric parameters (Å,°) for **2b**.

Cu1 – O4′	1.911(4)	O1′ – Cu1 – O5	84.04 (16)
Cu1 – O4	1.911(4)	O1′ – Cu1 – O5′	95.96 (16)
Cu1 – O5	1.923(4)	O1 – Cu1 – O4	60.87 (16)
Cu1 – O5′	1.923(4)	O1 – Cu1 – O4′	119.13 (16)
Cu1 – O1	3.088(5)	O1 – Cu1 – O5	95.96 (16)
Cu1 – O1′	3.088(5)	O1 – Cu1 – O5′	84.04 (16)
Cu2 – O4	1.964(4)	O1 – Cu1 – O1′	180.00 (10)
Cu2 – O1	1.974(5)	O4 – Cu2 – O1	87.69(18)
Cu2 – N1	2.015(6)	O4 – Cu2 – N1	92.7(2)
Cu2 – N2	2.017(5)	O4 – Cu2 – N2	169.43(19)
Cu2 – O3	2.288(5)	O4 – Cu2 – O3	81.65(17)
		O1 – Cu2 – N1	175.9(2)
O4′ – Cu1 – O4	180.0	O1 – Cu2 – N2	92.4(2)
O4′ – Cu1 – O5	93.74(18)	O1 – Cu2 – O3	76.65(18)
O4′ – Cu1 – O5′	86.26(18)	N1 – Cu2 – N2	87.8(2)
O4 – Cu1 – O5	86.26(18)	N1 – Cu2 – O3	99.4(2)
O4 – Cu1 – O5′	93.74(18)	N2 – Cu2 – O3	108.66(18)
O5 – Cu1 – O5′	180.0(3)		
O1′ – Cu1 – O4	119.13(16)		
O1′ – Cu1 – O4′	60.87(16)		

′ = -*x*, -*y*+2, -*z*+1

Table S6. Selected geometric parameters (Å,°) for **2c**.

Cu1 – O1	1.9739(14)	O1 – Cu1 – O3′	85.76(6)
Cu1 – O1′	1.9740(14)	O1′ – Cu1 – N1	90.48(7)
Cu1 – N1	2.0556(16)	O1′ – Cu1 – N1′	174.94(5)
Cu1 – N1′	2.0557(16)	O1′ – Cu1 – O3	85.75(6)
Cu1 – O3	2.365(2)	O1′ – Cu1 – O3′	75.61(5)
Cu1 – O3′	2.365(2)	N1 – Cu1 – N1′	85.88(9)
		N1 - Cu1 - O3	101.43 (6)
O1 – Cu1 – O1′	93.37(9)	N1 – Cu1 – O3′	98.40 (6)
O1 – Cu1 – N1	174.94(5)	N1′ – Cu1 – O3	98.40 (6)
O1 – Cu1 – N1′	90.48(7)	N1′ – Cu1 – O3′	101.43 (6)
O1 – Cu1 – O3	75.61(5)	O3 – Cu1 – O3′	152.79 (6)

′ = -*x*+3/2, -*y*+3/2, *z*; ″= -*x*+1/2, -*y*+3/2, *z*

Table S7. Selected geometric parameters (Å,°) for **3a**.

Cu1 – O10	1.939(2)	O10 – Cu1 – O11	169.25(12)
Cu1 – O1	1.950(2)	O10 – Cu1 – O9	92.91(14)
Cu1 – O8″	1.958(2)	O1 – Cu1 – O8″	172.98(11)
Cu1 – O11	1.961(3)	O1 – Cu1 – O11	86.93(9)
Cu1 – O9	2.227(3)	O1 – Cu1 – O9	96.00(11)
		O8″ – Cu1 – O11	92.61(9)
O10 – Cu1 – O1	91.15(9)	O8″ – Cu1 – O9	91.00(11)
O10 – Cu1 – O8″	88.01(9)	O11 – Cu1 – O9	97.81(14)

′ = *x*+1, *y*, *z*; ″= *x*-1, *y*, *z*

Table S8. Hydrogen-bond geometry (Å,°) in **1**.

Donor–H···Acceptor	D–H	H···A	D···A	D–H···A
N1–H1O···O3′	0.91	2.13	3.033(7)	170
N1–H1P···O1″	0.91	2.09	2.988(8)	169
N3–H3O···O4‴	0.91	1.97	2.864(6)	167
N3–H3P···O4″″	0.91	2.06	2.914(7)	155
O5–H5O···O1′	0.89(3)	2.03(5)	2.809(6)	146(6)
O5–H5P···O3‴	0.90(5)	1.91(6)	2.760(6)	156(6)
O6–H6O···O2	0.90	1.90	2.795(18)	179
O7–H7O···O2	0.90	1.91(4)	2.811(12)	162

′= 3/2-*x*-1,-1/2+*y*,1-*z*; ″ = 3/2-*x*,1/2+*y*,1-*z*; ‴=*x*,-1+*y*,*z*; ″″=3/2-*x*,-1/2+*y*,-*z*

Table S9. Hydrogen-bond geometry (Å,°) in **2a**.

Donor—H···Acceptor	D–H	H···A	D···A	D–H···A
O3–H3O···O8	0.84(3)	1.87(5)	2.70(3)	165(8)
O4–H4O···O7	0.85(4)	1.92(4)	2.71(3)	155(7)
O7–H7O···O5′	0.86(7)	1.89(7)	2.75(3)	176(10)
O7–H7P···O2	0.87(8)	2.04(8)	2.87(3)	159(7)
O8–H8O···O5	0.85(7)	2.36(9)	2.89(4)	121(7)
O8–H8P···O2″	0.84(7)	1.90(8)	2.73(3)	168(8)

′=-*x*,-1/2+*y*,2-*z*; ″=1-*x*,1/2+*y*,2-*z*

Table S10. Hydrogen-bond geometry (Å,°) in **2b**.

Donor—H···Acceptor	D–H	H···A	D···A	D–H···A
O3–H3O···O7	0.84(5)	1.76(5)	2.587(7)	165(7)
O7–H7O···O6′	0.86(8)	1.85(8)	2.687(7)	163(6)
O7–H7P···O2″	0.85(8)	1.84(8)	2.685(8)	173(7)

′=1/2+*x*,3/2-*y*,1/2+*z*; ″=1+*x*,*y*,*z*

Table S11. Hydrogen-bond geometry (Å,°) in **2c**.

Donor–H···Acceptor	D–H	H···A	D···A	D–H···A
O3–H3O···O4	0.83(2)	1.86(2)	2.681(2)	171(3)
O3–H3O···O5′	0.83(2)	1.90(2)	2.688(12)	159(3)
O4–H4O···O2′	0.80	1.92	2.722(3)	180
O4–H4P···O2″	0.87	2.08	2.945(3)	179

′=1-*x*,1/2+*y*,3/2-*z*; ″=1/2-*x*,3/2-*y*,*z*

Table S12. Hydrogen-bond geometry (Å,°) in **3a**.

Donor—H···Acceptor	D–H	H···A	D···A	D–H···A
O9–H9···O4′	0.85	2.09	2.935(5)	180
O10–H10O···O2	0.86(4)	2.10(4)	2.737(3)	130(5)
O10–H10O···O5″	0.86(4)	2.48(6)	2.927(3)	113(4)
O10–H10P···O7″	0.91(4)	1.80(4)	2.704(3)	171(5)
O11–H11O···O7′	0.92(4)	1.79(4)	2.611(3)	147(5)
O11–H11P···O2‴	0.92(5)	1.81(4)	2.720(3)	171(4)

′=-1+*x*,*y*,*z*; ″=1-*x*,1/2+*y*,1-*z*; ‴=1-*x*,-1/2+*y*,1-*z*

S1.2. Supplementary Figures

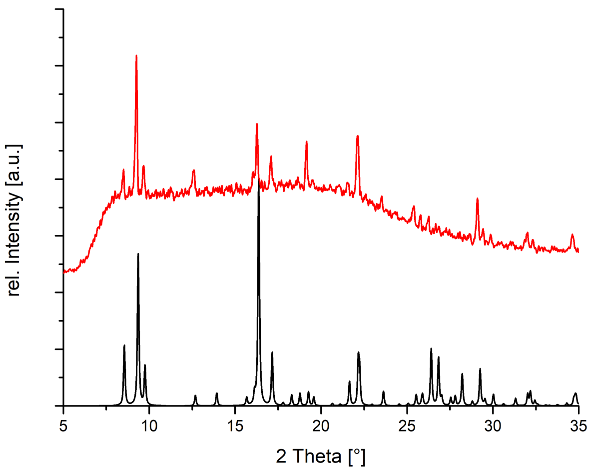

Figure S1. Measured (red) and calculated (black) powder diffraction pattern for **1**.

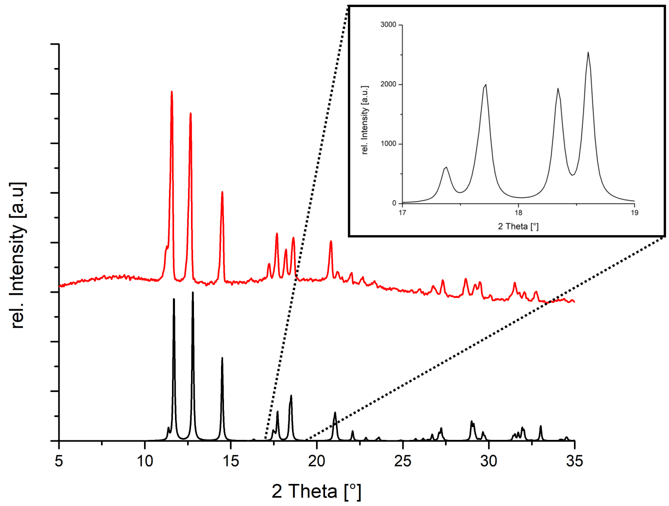

Figure S2. Experimental (red) and calculated (black) powder patterns for **2a**. The calculated pattern is based on the single crystal diffraction experiment at low temperature. A slight increase of the angle βat higher temperature will result in a split of the reflections at 17-19° as shown in the inlay.

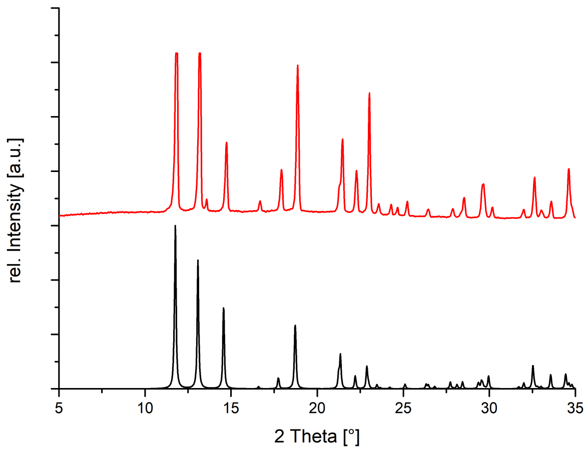

Figure S3. Measured (red) and calculated (black) powder diffraction pattern for **2c**.

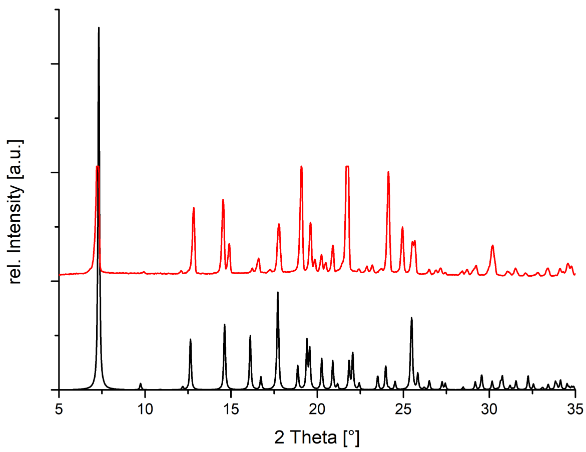

Figure S4. Measured (red) and calculated (black) powder diffraction pattern for **3a**.

S1.3. Refinement Details

S1.3.1. Compound **1**:

The hydrogen atoms of the aqua ligand were treated as riding on O, with O–H and H···H restrained to 0.9 Å and 1.45 Å respectively. U_{iso} for the hydrogen atoms were refined freely. The hydrogen atoms attached to nitrogen were located from the difference Fourier map and refined as riding with $U_{iso}(H) = 1.2 \times U_{eq}(N)$. For the co-crystallized water molecules, hydrogen atoms were introduced into positions along the shortest observed hydrogen bonds, where they were constrained as riding on O. The two water sites were not mutually exclusive; their occupancies were refined independently, leading to a content of approximately 2.4 co-crystallized water molecules per unit cell. Refinement of these water molecules as mutually exclusive, with a total occupancy constrained to unity was attempted as well as refinement of the structure as a pseudo-merohedral monoclinic twin. Neither of these measures increased the quality of the refinement significantly.

S1.3.2. Compound **2a**:

The hydrogen atoms bonded to oxygen both in the free water molecules and in the hydroxy groups were located from the difference Fourier map and their coordinates were refined freely with O–H restrained to 0.85 Å and $U_{iso}(H) = 1.2 \times U_{eq}(O)$. The structure was refined as a two-domain pseudo-merohedral ($\beta = 90°$) twin with the twin law $\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$ and relative domain fractions of 0.79(3) and 0.21(3).

S1.3.3. Compound **2b**:

The hydrogen atoms associated with the uncoordinated water molecule and the coordinating hydroxy group were placed between their parent oxygen atom and the geometrically best fitting H-bond acceptor. Their positional coordinates were freely refined with a distance restraint O–H = 0.85 Å, with $U_{iso}(H) = 1.2 \times U_{eq}(O)$.

The structure was refined as a pseudo-merohedral twin $\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$ with relative domain fractions of 0.30(2) and 0.70(2). The H atom of the bridging hydroxy group was introduced into a calculated position and refined as riding on the parent O atom. The occupancy of this H atom was set to 0.5, in agreement with the oxidation state +I of the central copper atom, see susceptibility measurements in Section 2.3.

S1.3.4. Compound **2c**:

The hydrogen atom associated with the hydroxy group in **2c** was located from the difference Fourier map and refined without restraints with $U_{iso}(H) = 1.2 \times U_{eq}(O)$. **2c** contains a co-crystallized water molecule, disordered about two mutually exclusive positions. Their site occupancies were refined and the sum of the occupancies was constrained to unity. The H atoms of the solvent water molecules were refined as riding. Their coordinates were calculated to fit the observed hydrogen bonds in the structure. A tentative refinement with restrained O–H and H···H distances led to inferior results and an unsatisfactory hydrogen bond geometry.

S1.3.5. Compound **3a**:

The coordinates of the hydrogen atoms associated with the two coordinated water molecules were obtained from the difference Fourier map. They were refined with a distance restraint of O–H = 0.9 Å and $U_{iso}(H)$ constrained to $1.2 \times U_{eq}(O)$. A strongly prolate displacement parameter for the terminal carbon atom of the ethanol molecule indicated positional disorder. The occupancy for the mutually exclusive positions refined to a ratio of 0.69(3):0.31(3). Both partially occupied sites were refined isotropically.