Robustness and stability of the L-carnosine copper(II) dimer. Changes in the copper coordination sphere upon heating/solvent substitution

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Supplementary Materials

Table S1. Bond lengths for $\mathbf{1}_{170}$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	O1	1.982(3)	N2	C5	1.455(5)
Cu1	OW1	2.405(5)	N3	C8	1.372(5)
Cu1	N1A	2.019(5)	N3	C9	1.315(5)
Cu1	N1B	2.009(7)	N4	C7	1.368(5)
Cu1	N2	1.953(3)	N4	C9	1.341(4)
Cu1	$N3^1$	1.998(3)	C1A	C2A	1.526(13)
O1	C4	1.275(4)	C1B	C2B	1.47(3)
O2	C4	1.235(5)	C2A	C3A	1.518(7)
O3A	C3A	1.269(5)	C2B	C3B	1.509(8)
O3B	C3B	1.262(6)	C4	C5	1.526(5)
N1A	C1A	1.487(7)	C5	C6	1.541(5)
N1B	C1B	1.486(8)	C6	C7	1.496(5)
N2	C3A	1.346(6)	C7	C8	1.362(4)
N2	C3B	1.326(7)			

Symmetry code: ^{1}*-x,-x+y,4/3-z*

Table S2. Bond angles for $\mathbf{1}_{170}$.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
O1	Cu1	OW1	90.27(12)	C9	N3	C8	105.8(3)
O1	Cu1	N1A	173.2(3)	C9	N4	C7	108.9(3)
O1	Cu1	N1B	164.8(5)	N1A	C1A	C2A	111.2(9)
O1	Cu1	$N3^1$	88.53(12)	C2B	C1B	N1B	115(2)
N1A	Cu1	OW1	92.3(3)	C3A	C2A	C1A	116.6(8)
N1B	Cu1	OW1	75.9(4)	C1B	C2B	C3B	116.5(12)
N2	Cu1	O1	82.68(12)	O3A	C3A	N2	123.1(6)
N2	Cu1	OW1	109.07(12)	O3A	C3A	C2A	113.6(6)
N2	Cu1	N1A	90.5(3)	N2	C3A	C2A	123.2(5)
N2	Cu1	N1B	95.8(4)	O3B	C3B	N2	122.7(10)
N2	Cu1	$N3^1$	155.85(13)	O3B	C3B	C2B	126.3(9)
$N3^1$	Cu1	OW1	93.35(12)	N2	C3B	C2B	110.1(6)
$N3^1$	Cu1	N1A	97.6(3)	O1	C4	C5	117.2(4)
$N3^1$	Cu1	N1B	98.3(5)	O2	C4	O1	122.8(4)
C4	O1	Cu1	113.4(2)	O2	C4	C5	119.9(3)
C1A	N1A	Cu1	112.7(10)	N2	C5	C4	109.1(3)
C1B	N1B	Cu1	108.5(13)	N2	C5	C6	110.6(3)
C3A	N2	Cu1	129.7(3)	C4	C5	C6	110.8(3)
C3A	N2	C5	118.6(3)	C7	C6	C5	113.5(3)
C3B	N2	Cu1	130.4(5)	N4	C7	C6	123.5(3)
C3B	N2	C5	114.0(5)	C8	C7	N4	104.5(3)
C5	N2	Cu1	111.1(2)	C8	C7	C6	132.0(3)
C8	N3	$Cu1^1$	124.7(2)	C7	C8	N3	110.3(3)
C9	N3	$Cu1^1$	129.4(3)	N3	C9	N4	110.5(4)

Symmetry code: ^{1}*-x,-x+y,4/3-z*

Table S3. Hydrogen bonds for $\mathbf{1}_{170}$.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
OW1	HW1A	OW2[1]	0.87	1.87	2.734(4)	171.4
OW1	HW1B	O1[2]	0.87	2.14	2.999(4)	171.1
OW2	HW2A	O2[3]	0.87	1.91	2.742(5)	159.6
OW2	HW2B	O3A	0.87	1.83	2.702(8)	178.3
OW2	HW2B	O3B	0.87	2.01	2.847(12)	161.3
N1A	H1AA	OW1[2]	0.91	2.18	2.997(9)	148.1
N1B	H1BB	OW1[2]	0.91	2.23	2.961(13)	136.8
N4	H4	O3A[4]	0.88	1.87	2.728(9)	165.7
N4	H4	O3B[4]	0.88	1.79	2.661(13)	169.7

Symmetry code: [1]*+y,1+x,1-z*; [2]*1-x,-x+y,4/3-z*; [3]*-1+y,1+x,1-z*; [4]*-1+y,+x,1-z*

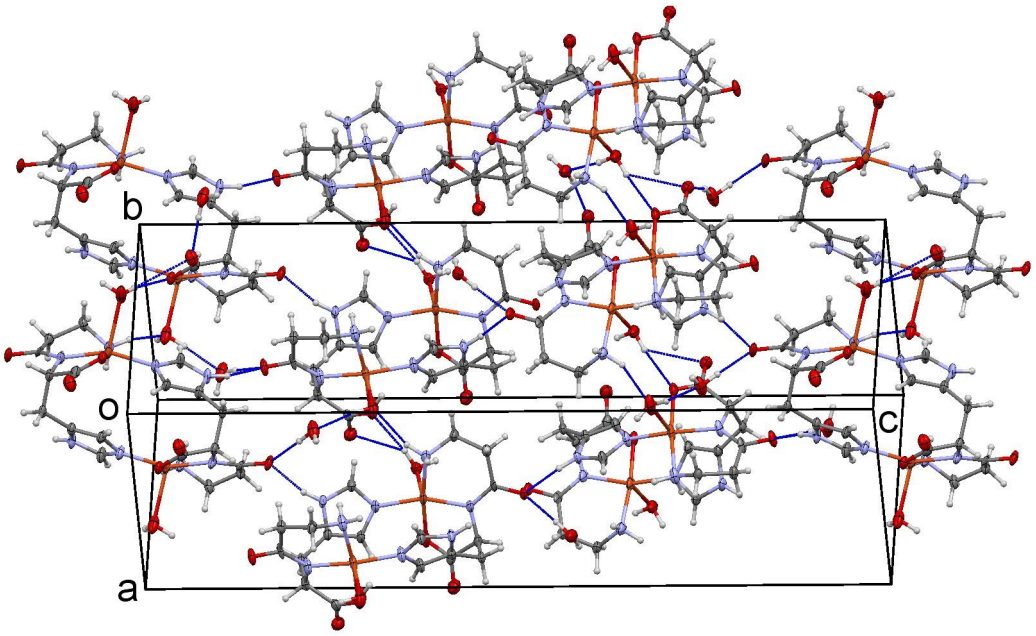

Figure S1. Packing of the complex and water molecules of **1** at 170 K. Hydrogen bonds are shown by blue lines.

Table S4. Bond lengths for $\mathbf{1_{270}}$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	O1	1.978(3)	N2	C5	1.456(4)
Cu1	N1A	2.017(6)	N3	C8	1.372(5)
Cu1	N1B	2.012(6)	N3	C9	1.316(5)
Cu1	N2	1.948(2)	N4	C7	1.364(5)
Cu1	N3[1]	1.998(2)	N4	C9	1.341(4)
O1	C4	1.277(4)	C1A	C2A	1.511(17)
O2	C4	1.233(5)	C1B	C2B	1.49(3)
O3A	C3A	1.261(6)	C2A	C3A	1.529(8)
O3B	C3B	1.255(6)	C2B	C3B	1.521(8)
N1A	C1A	1.487(8)	C4	C5	1.523(5)
N1B	C1B	1.487(8)	C5	C6	1.530(5)
N2	C3A	1.337(6)	C6	C7	1.498(5)
N2	C3B	1.325(6)	C7	C8	1.366(4)

Symmetry code: [1]*-x,-x+y,4/3-z*

Table S5. Bond angles for $\mathbf{1_{270}}$.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
O1	Cu1	N1A	172.6(4)	N1B	C1B	C2B	114.2(19)
O1	Cu1	N1B	165.3(5)	C1A	C2A	C3A	115.1(10)
O1	Cu1	N3[1]	88.45(12)	C1B	C2B	C3B	115.9(11)
N2	Cu1	O1	82.72(11)	O3A	C3A	N2	122.7(9)
N2	Cu1	N1A	89.9(4)	O3A	C3A	C2A	112.9(8)
N2	Cu1	N1B	96.1(4)	N2	C3A	C2A	124.4(6)
N2	Cu1	N3[1]	155.80(13)	O3B	C3B	N2	125.3(10)
N3[1]	Cu1	N1A	98.2(4)	O3B	C3B	C2B	124.0(9)
N3[1]	Cu1	N1B	97.9(4)	N2	C3B	C2B	110.5(6)
C4	O1	Cu1	113.3(2)	O1	C4	C5	117.2(3)
C1A	N1A	Cu1	113.3(12)	O2	C4	O1	122.4(3)
C1B	N1B	Cu1	109.3(12)	O2	C4	C5	120.3(3)
C3A	N2	Cu1	129.3(4)	N2	C5	C4	108.9(3)
C3A	N2	C5	119.0(4)	N2	C5	C6	111.3(3)
C3B	N2	Cu1	131.5(4)	C4	C5	C6	111.0(3)
C3B	N2	C5	114.3(4)	C7	C6	C5	113.7(3)
C5	N2	Cu1	111.18(19)	N4	C7	C6	123.7(3)
C8	N3	Cu1[1]	124.3(2)	N4	C7	C8	104.7(3)
C9	N3	Cu1[1]	129.6(3)	C8	C7	C6	131.6(3)
C9	N3	C8	106.0(3)	C7	C8	N3	110.0(3)
C9	N4	C7	108.9(3)	N3	C9	N4	110.4(3)
N1A	C1A	C2A	110.5(11)				

Symmetry code: [1]*-x,-x+y,4/3-z*

Table S6. Hydrogen bonds for $\mathbf{1_{270}}$.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
OW1	HW1A	OW2[1]	0.87	1.88	2.737(5)	166.7
OW1	HW1B	O1[2]	0.87	2.15	3.022(4)	173.5
OW2	HW2A	O2[3]	0.87	1.92	2.726(6)	151.9
OW2	HW2B	O3A	0.87	1.86	2.714(10)	165.3
OW2	HW2B	O3B	0.87	2.03	2.820(12)	149.1
N1A	H1AA	OW1[2]	0.89	2.22	3.011(11)	148.0
N1B	H1BB	OW1[2]	0.89	2.23	2.958(13)	139.4
N4	H4	O3A[4]	0.86	1.91	2.753(12)	165.7
N4	H4	O3B[4]	0.86	1.79	2.645(14)	171.6

Symmetry code: [1]*+y,1+x,1-z*; [2]*1-x,-x+y,4/3-z;* [3]*-1+y,1+x,1-z;* [4]*-1+y,+x,1-z*

Table S7. Bond lengths for $\mathbf{1}_{370}$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	O1	1.899(12)	N4	C9	1.350(18)
Cu1	N2	1.912(6)	N1A	C1A	1.51(3)
Cu1	N3[1]	1.991(7)	C1A	C2A	1.57(5)
Cu1	N1A	1.960(15)	C2A	C3A	1.47(2)
Cu1	N1B	1.960(16)	C3A	O3A	1.247(14)
O1	C4	1.299(18)	N1B	C1B	1.51(3)
O2	C4	1.189(18)	C1B	C2B	1.48(7)
N2	C3A	1.357(15)	C2B	C3B	1.47(2)
N2	C3B	1.361(15)	C3B	O3B	1.248(14)
N2	C5	1.422(15)	C4	C5	1.55(2)
N3	C8	1.348(18)	C5	C6	1.482(19)
N3	C9	1.333(17)	C6	C7	1.489(19)
N4	C7	1.36(2)	C7	C8	1.368(12)

Symmetry code: [1]*+y,+x,1-z*

Table S8. Bond angles for $\mathbf{1}_{370}$.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
O1	Cu1	N2	83.0(4)	N2	C3A	C2A	112.7(14)
O1	Cu1	N3[1]	89.2(4)	O3A	C3A	N2	119.7(17)
O1	Cu1	N1A	161.8(17)	O3A	C3A	C2A	127.1(17)
O1	Cu1	N1B	165.7(16)	C1B	N1B	Cu1	119(3)
N2	Cu1	N3[1]	159.6(4)	C2B	C1B	N1B	106(4)
N2	Cu1	N1A	99.4(8)	C3B	C2B	C1B	115(3)
N2	Cu1	N1B	89.5(9)	N2	C3B	C2B	121.2(18)
N1A	Cu1	N3[1]	93.9(10)	O3B	C3B	N2	127(2)
N1B	Cu1	N3[1]	101.7(11)	O3B	C3B	C2B	112(2)
C4	O1	Cu1	115.6(10)	O1	C4	C5	112.9(13)
C3A	N2	Cu1	129.1(9)	O2	C4	O1	124.7(14)
C3A	N2	C5	117.2(10)	O2	C4	C5	122.0(15)
C3B	N2	Cu1	130.6(10)	N2	C5	C4	109.0(10)
C3B	N2	C5	115.0(11)	N2	C5	C6	112.7(12)
C5	N2	Cu1	111.1(6)	C6	C5	C4	110.7(11)
C8	N3	Cu1[1]	121.8(7)	C5	C6	C7	114.2(9)
C9	N3	Cu1[1]	131.6(11)	N4	C7	C6	125.1(10)
C9	N3	C8	106.3(10)	N4	C7	C8	103.3(13)
C9	N4	C7	110.3(10)	C8	C7	C6	131.4(16)
C1A	N1A	Cu1	105(2)	N3	C8	C7	111.5(13)
N1A	C1A	C2A	112(4)	N3	C9	N4	108.5(15)
C3A	C2A	C1A	113(2)				

Symmetry code: [1]*+y,+x,1-z*

Table S9. Hydrogen bonds for $\mathbf{1}_{370}$ and short contacts involving O1W.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N4	H4	O3A[1]	0.86	1.80	2.65(2)	171.6
N4	H4	O3B[1]	0.86	1.96	2.78(3)	158.7
N1A	H1AA	O1[2]	0.89	2.37	3.06(4)	134.8
N1A	H1AB	O1W	0.89	2.16	3.02(5)	162.6
O1W		O2[3]			2.81(4)	
O1W		O1[3]			2.95(5)	

Symmetry code: [1]*-y+x,1-y,2/3-z;* [2]*+y,-1+x,1-z;* [3]*x,1+y,z*

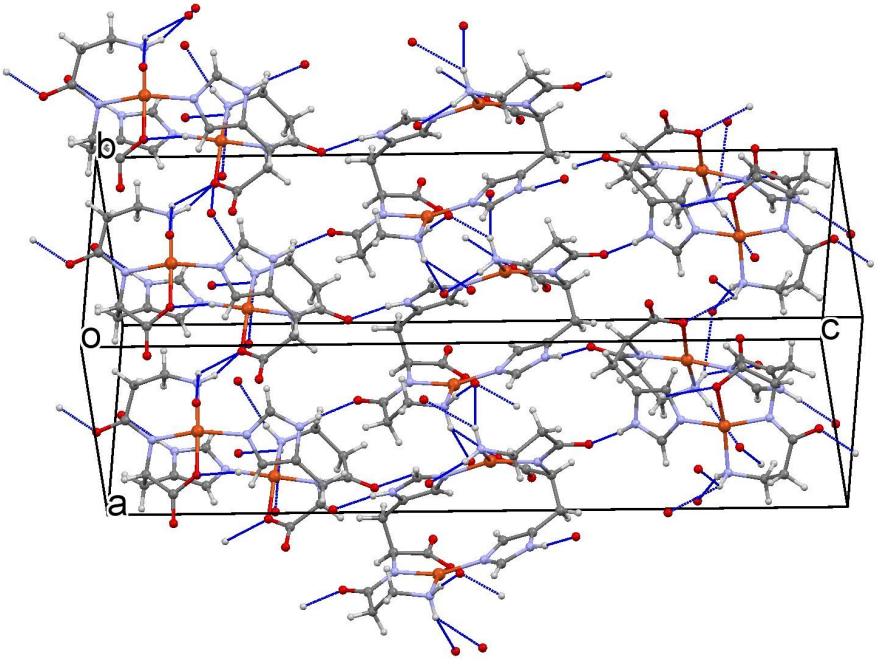

Figure S2. Packing of the complex and water molecules of **1** at 370 K. Hydrogen bonds are shown by blue lines.

Table S10. Selected IR spectral bands (cm^{-1}) of the carnosine and **1.**

Assignment	ν, cm^{-1}	
	carnosine	1
ν (NH_2), ν(OH)	3240	3300
ν (NHCO)	1655	1627
$\nu_{as}(COO^-)$	1564	1560
$\nu_s(COO^-)$	1403	1395

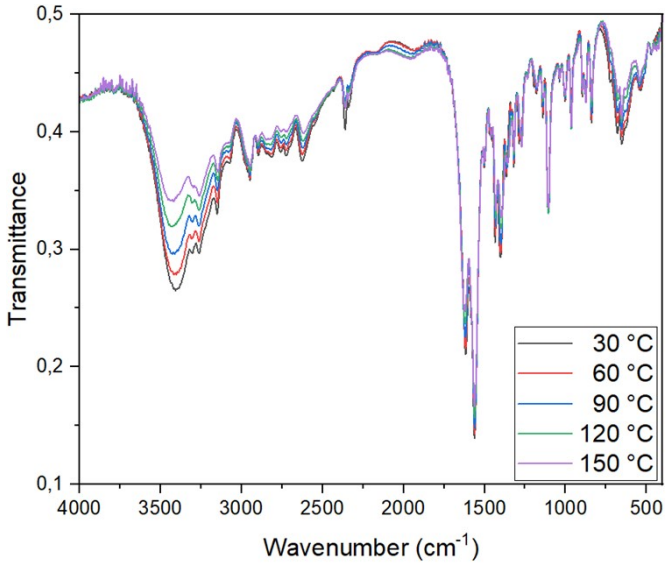

Figure S3. Variable temperature FTIR spectra of compound **1**.

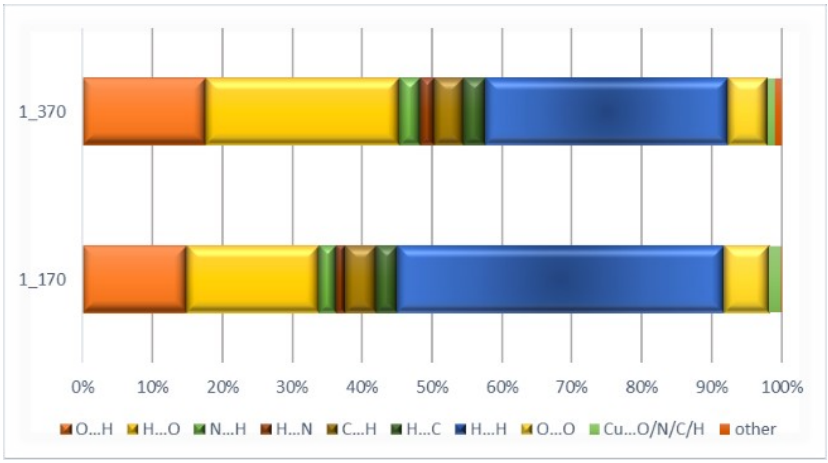

Diagram S1. Distribution of intermolecular contacts based on HS analysis for structures $\mathbf{1_{170}}$ and $\mathbf{1_{370}}$.

Table S11. Bond lengths for $\mathbf{2_{100}}$ (solvent masking).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu	O1	1.9849(16)	N3	C9	1.329(3)
Cu	N1	1.993(2)	N4	C7	1.386(3)
Cu	N2	1.9387(19)	N4	C9	1.338(3)
Cu	N3[1]	1.9658(19)	C1	C2	1.501(5)
O1	C4	1.262(3)	C2	C3	1.515(4)
O2	C4	1.260(3)	C4	C5	1.524(3)
O3	C3	1.266(3)	C5	C6	1.556(3)
N1	C1	1.476(3)	C6	C7	1.492(3)
N2	C3	1.311(3)	C7	C8	1.369(3)
N2	C5	1.451(3)	O4	C10	1.468(7)
N3	C8	1.386(3)			

Symmetry code: [1]*1-x,+y,1-z*

Table S12. Bond angles for $\mathbf{2_{100}}$ (solvent masking).

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
O1	Cu	N1	168.08(10)	C1	C2	C3	116.9(2)
N2	Cu	O1	84.06(7)	O3	C3	N2	123.4(3)
N2	Cu	N1	94.35(9)	O3	C3	C2	118.0(2)
N2	Cu	N3[1]	159.59(9)	N2	C3	C2	118.6(2)
N3[1]	Cu	O1	92.52(7)	O1	C4	C5	118.1(2)
N3[1]	Cu	N1	92.96(9)	O2	C4	O1	124.0(2)
C4	O1	Cu	113.48(15)	O2	C4	C5	117.7(2)
C1	N1	Cu	112.70(17)	N2	C5	C4	108.90(18)
C3	N2	Cu	131.42(18)	N2	C5	C6	111.8(2)
C3	N2	C5	116.8(2)	C4	C5	C6	107.10(19)
C5	N2	Cu	111.40(14)	C7	C6	C5	111.45(18)
C8	N3	Cu[1]	129.51(16)	N4	C7	C6	122.0(2)
C9	N3	Cu[1]	124.54(15)	C8	C7	N4	105.42(18)
C9	N3	C8	105.86(18)	C8	C7	C6	132.3(2)
C9	N4	C7	108.13(18)	C7	C8	N3	109.49(19)
N1	C1	C2	112.6(3)	N3	C9	N4	111.10(19)

Symmetry code: [1]*1-x,+y,1-z*

Table S13. Hydrogen bonds for $\mathbf{2_{100}}$ (solvent masking).

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N1	H1A	O3[1]	0.91	2.15	2.990(4)	152.9
N4	H4	O2[2]	0.88	1.83	2.690(3)	167.1
O4	H4A	O3[1]	0.84	1.83	2.655(3)	168.5

Symmetry code: [1]*1/2+x,3/2-y,3/2-z*; [2]*+x,1-y,1-z*

Table S14. Atomic occupancy for $\mathbf{2_{100}}$ (solvent masking).

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
O2W	0.297(14)	C10	0.703(14)	H10A	0.703(14)
H10B	0.703(14)	H10C	0.703(14)		

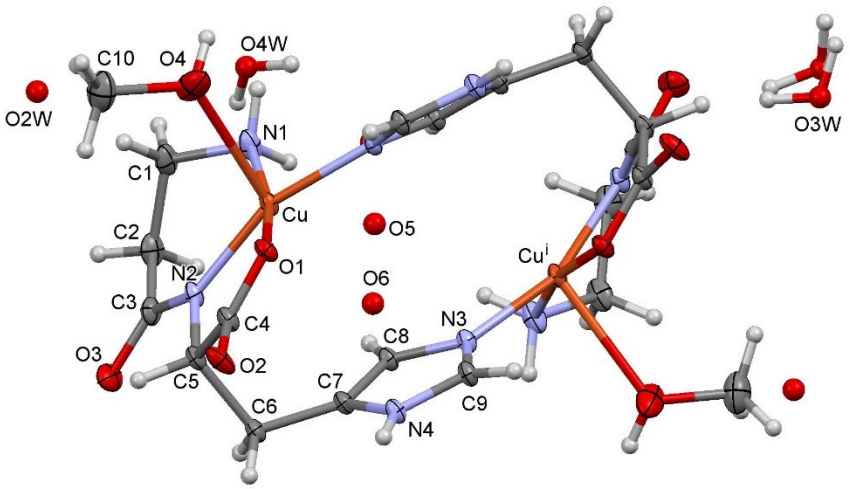

Figure S4. Structure of **2** at 100 K (some solvent atoms found) with the atom numbering scheme. The apical position in $\mathbf{2}_{100}$ is occupied by either a methanol molecule (occupancy of 0.654(14) for O4 and C10) or two water molecules (occupancy of 0.346(14) for O4 and OW2). Therefore, when O4 is a water molecule bonded to Cu(II), it is hydrogen bonded to a solvent water molecule OW2. Four O atoms were found in the structure of $\mathbf{2}_{100}$, O3W, O4W, O5 and O6, of which O3W and O6 are disordered over two-fold symmetry-related sites, while O4W and O5 are positioned on two-fold axes. Since O5 and O6 are too close, either O5 or O6 (occupancy of 0.25) is present. For O3W and O4W, hydrogen atoms could be placed, but not for other O atoms. There is still 465.1 Å^3 of potential solvent accessible area, probably due to disordered methanol molecules.

Table S15. Bond lengths for $\mathbf{2}_{100}$ (some solvent atoms found).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu	O1	1.9854(15)	N4	C7	1.379(3)
Cu	N1	1.993(2)	N4	C9	1.342(2)
Cu	N2	1.9375(17)	C1	C2	1.505(5)
Cu	N3^1	1.9657(17)	C2	C3	1.510(4)
O1	C4	1.269(2)	C4	C5	1.521(3)
O2	C4	1.251(3)	C5	C6	1.555(3)
O3	C3	1.267(3)	C6	C7	1.490(3)
N1	C1	1.480(3)	C7	C8	1.372(3)
N2	C3	1.313(3)	O4	C10	1.481(6)
N2	C5	1.461(3)	O3W	O3W^2	1.606(11)
N3	C8	1.384(2)	O6	O5	1.318(16)
N3	C9	1.327(3)			

Symmetry code: ^{1}*1-x,+y,1-z*; ^{2}*-x,1-y,+z*

Table S16. Bond angles for $\mathbf{2_{100}}$ (some solvent atoms found).

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
O1	Cu	N1	168.06(8)	O3	C3	N2	123.3(2)
N2	Cu	O1	84.06(7)	O3	C3	C2	118.1(2)
N2	Cu	N1	94.38(8)	N2	C3	C2	118.6(2)
N2	Cu	N3[1]	159.67(8)	O1	C4	C5	118.12(18)
N3[1]	Cu	O1	92.52(6)	O2	C4	O1	124.05(19)
N3[1]	Cu	N1	92.92(8)	O2	C4	C5	117.65(18)
C4	O1	Cu	113.53(13)	N2	C5	C4	108.73(16)
C1	N1	Cu	112.76(16)	N2	C5	C6	111.63(17)
C3	N2	Cu	131.44(16)	C4	C5	C6	107.19(17)
C3	N2	C5	116.65(18)	C7	C6	C5	111.73(16)
C5	N2	Cu	111.48(12)	N4	C7	C6	122.25(17)
C8	N3	Cu[1]	129.56(14)	C8	C7	N4	105.34(16)
C9	N3	Cu[1]	124.42(14)	C8	C7	C6	132.09(18)
C9	N3	C8	105.92(16)	C7	C8	N3	109.48(17)
C9	N4	C7	108.35(16)	N3	C9	N4	110.91(17)
N1	C1	C2	112.4(2)	O6[1]	O5	O6	161.7(12)
C1	C2	C3	117.1(2)				

Symmetry code: [1]*1-x,+y,1-z*

Table S17. Hydrogen bonds for $\mathbf{2_{100}}$ (some solvent atoms found).

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N1	H1A	O3[1]	0.91	2.14	2.984(3)	153.0
N1	H1B	O6[2]	0.91	2.06	2.895(7)	152.7
N4	H4	O2[3]	0.88	1.83	2.698(3)	167.0
O4	H4A	O3[1]	0.84	1.93	2.655(3)	144.6
O3W	H3WA	O2	0.876(5)	1.8644(17)	2.689(5)	156.0(4)
O3W	H3WB	O2[4]	0.872(5)	1.8678(17)	2.721(5)	165.8(4)
O4W	H4W	O4[3]	0.885(4)	2.240(3)	2.918(3)	133.2(3)

Symmetry code: [1]*1/2+x,3/2-y,3/2-z*; [2]*1-x,+y,1-z*; [3]*+x,1-y,1-z*; [4]*-x,1-y,+z*

Table S18. Atomic occupancy for $\mathbf{2_{100}}$ (some solvent atoms found).

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
O2W	0.346(14)	C10	0.654(14)	H10A	0.654(14)
H10B	0.654(14)	H10C	0.654(14)	O3W	0.5
H3WA	0.5	H3WB	0.5	O6	0.5
O5	0.5				

Table S19. Bond lengths for $\mathbf{2_{170}}$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	O1	1.9827(19)	N4	C7	1.381(3)
Cu1	N1	1.990(3)	N4	C9	1.328(4)
Cu1	N2	1.944(2)	N3	C8	1.381(4)
Cu1	N3[1]	1.972(2)	N3	C9	1.323(4)
O1	C4	1.276(3)	C1	C2	1.516(6)
O2	C4	1.247(4)	C2	C3	1.516(5)
O3	C3	1.258(4)	C4	C5	1.514(4)
N1	C1	1.484(4)	C5	C6	1.551(4)
N2	C3	1.311(4)	C6	C7	1.502(4)
N2	C5	1.457(4)	C7	C8	1.362(4)

Symmetry code: [1]*1-x,1-y,+z*

Table S20. Bond angles for $\mathbf{2_{170}}$.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
O1	Cu1	N1	167.58(11)	C1	C2	C3	117.9(3)
N2	Cu1	O1	83.99(9)	O3	C3	N2	123.7(3)
N2	Cu1	N1	94.74(11)	O3	C3	C2	117.9(3)
N2	Cu1	N3[1]	159.09(10)	N2	C3	C2	118.4(3)
N3[1]	Cu1	O1	92.46(9)	O1	C4	C5	117.7(3)
N3[1]	Cu1	N1	92.98(11)	O2	C4	O1	123.9(3)
C4	O1	Cu1	113.81(18)	O2	C4	C5	118.1(2)
C1	N1	Cu1	113.0(2)	N2	C5	C4	109.4(2)
C3	N2	Cu1	131.0(2)	N2	C5	C6	111.3(2)
C3	N2	C5	117.5(3)	C4	C5	C6	107.8(2)
C5	N2	Cu1	111.30(17)	C7	C6	C5	111.4(2)
C9	N4	C7	108.5(2)	N4	C7	C6	122.4(2)
C8	N3	Cu1[1]	128.84(19)	C8	C7	N4	105.0(2)
C9	N3	Cu1[1]	125.10(19)	C8	C7	C6	132.4(3)
C9	N3	C8	105.8(2)	C7	C8	N3	109.6(2)
N1	C1	C2	111.2(3)	N3	C9	N4	111.0(2)

Symmetry code: [1]*1-x,1-y,+z*

Table S21. Hydrogen bonds for $\mathbf{2_{170}}$.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N4	H4	O2[1]	0.88	1.85	2.714(3)	167.4
N1	H1A	O3[2]	0.91	2.18	3.017(4)	153.4
OW1	HW1A	O3[2]	0.87	2.11	2.669(3)	121.4

Symmetry code: [1]*+x,1-y,1-z;* [2]*1/2+x,1/2-y,3/2-z*

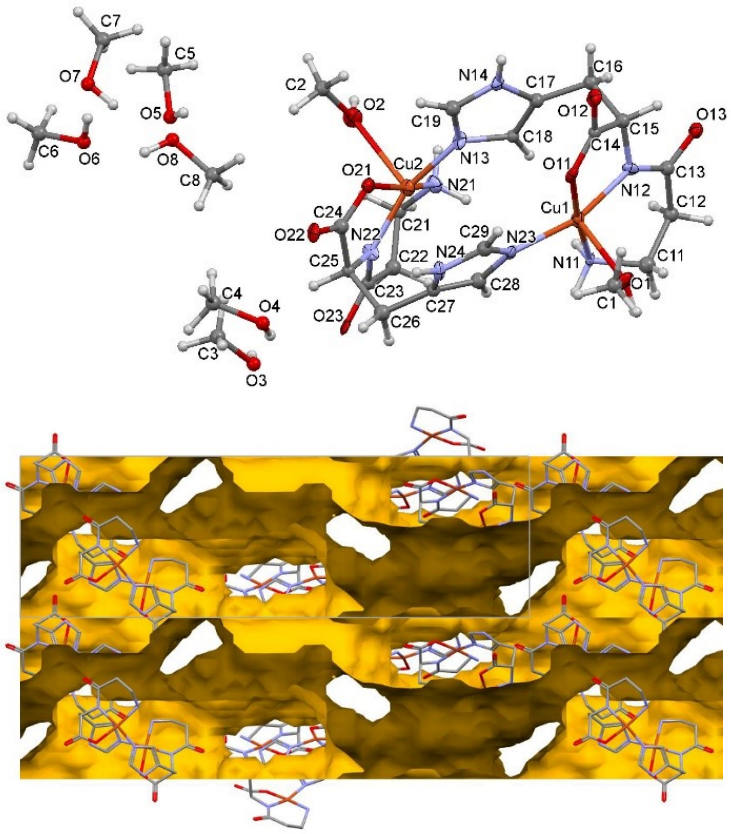

Figure S5. Structure of **3** at 150 K with the atom numbering scheme (top). View down the crystallographic *b*-axis showing an area occupied by MeOH molecules (orange color, bottom). Six solvent MeOH molecules could only be fitted into the electron density as rigid bodies. One of them, namely, C(6)O(6), is disordered over a two-fold axis and has an occupancy of 0.5. Hydrogen bonds shorter than 2.93 Å are N14–H14···O22 and N24–H24···O12 which link together two dimers. Only very weak hydrogen bonds link the dimers into a 3D hydrogen-bonded network.

Table S22. Bond lengths for **3.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	O1	2.392(14)	N21	C21	1.51(2)
Cu1	O11	1.959(13)	N22	C23	1.27(2)
Cu1	N11	2.030(15)	N22	C25	1.47(2)
Cu1	N12	1.948(15)	N23	C28	1.36(2)
Cu1	N23	1.964(16)	N23	C29	1.35(2)
Cu2	O2	2.393(15)	N24	C27	1.34(2)
Cu2	O21	1.969(14)	N24	C29	1.30(2)
Cu2	N13	1.951(16)	C11	C12	1.55(3)
Cu2	N21	1.991(17)	C12	C13	1.52(3)
Cu2	N22	1.935(15)	C14	C15	1.54(3)
O1	C1	1.409(17)	C15	C16	1.53(3)
O2	C2	1.402(17)	C16	C17	1.50(3)
O11	C14	1.23(2)	C17	C18	1.36(2)
O12	C14	1.22(2)	C21	C22	1.49(2)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O13	C13	1.24(2)	C22	C23	1.48(3)
O21	C24	1.29(2)	C24	C25	1.49(3)
O22	C24	1.26(2)	C25	C26	1.55(3)
O23	C23	1.26(2)	C26	C27	1.53(3)
N11	C11	1.48(2)	C27	C28	1.35(3)
N12	C13	1.36(2)	O3	C3	1.388(18)
N12	C15	1.46(2)	O4	C4	1.384(19)
N13	C18	1.43(2)	O5	C5	1.386(19)
N13	C19	1.30(2)	O7	C7	1.389(17)
N14	C17	1.41(2)	O8	C8	1.39(2)
N14	C19	1.37(2)	O6	C6	1.40(2)

Table S23. Bond angles for **3.**

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
O11	Cu1	O1	89.8(5)	C29	N23	Cu1	125.3(14)
O11	Cu1	N11	173.9(6)	C29	N23	C28	102.7(17)
O11	Cu1	N23	91.9(6)	C29	N24	C27	108.2(18)
N11	Cu1	O1	91.3(6)	N11	C11	C12	111.2(18)
N12	Cu1	O1	103.6(6)	C13	C12	C11	114.4(18)
N12	Cu1	O11	82.7(6)	O13	C13	N12	121.5(19)
N12	Cu1	N11	91.3(6)	O13	C13	C12	119.9(19)
N12	Cu1	N23	162.5(7)	N12	C13	C12	118.5(18)
N23	Cu1	O1	93.0(6)	O11	C14	C15	113.8(18)
N23	Cu1	N11	94.0(6)	O12	C14	O11	130(2)
O21	Cu2	O2	85.7(5)	O12	C14	C15	116.0(17)
O21	Cu2	N21	168.9(7)	N12	C15	C14	110.0(16)
N13	Cu2	O2	92.2(6)	N12	C15	C16	109.9(17)
N13	**Cu2**	O21	91.4(6)	C16	C15	C14	109.7(17)
N13	Cu2	N21	93.9(7)	C17	C16	C15	111.8(17)
N21	Cu2	O2	84.4(6)	N14	C17	C16	119.3(17)
N22	Cu2	O2	108.7(7)	C18	C17	N14	105.1(17)
N22	Cu2	O21	84.5(6)	C18	C17	C16	135(2)
N22	Cu2	N13	158.2(8)	C17	C18	N13	109.8(18)
N22	Cu2	N21	94.0(6)	N13	C19	N14	112(2)
C1	O1	Cu1	118.9(14)	C22	C21	N21	112.3(17)
C2	O2	Cu2	124.4(16)	C23	C22	C21	117.8(18)
C14	O11	Cu1	118.3(13)	O23	C23	N22	126(2)
C24	O21	Cu2	114.1(13)	O23	C23	C22	115.5(17)
C11	N11	Cu1	106.5(12)	N22	C23	C22	118.2(18)
C13	N12	Cu1	132.9(14)	O21	C24	C25	116.3(19)
C13	N12	C15	117.0(16)	O22	C24	O21	123.8(19)
C15	N12	Cu1	109.7(13)	O22	C24	C25	119.4(19)
C18	N13	Cu2	128.8(12)	N22	C25	C24	110.5(16)
C19	N13	Cu2	125.7(15)	N22	C25	C26	112.5(18)

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C19	N13	C18	105.5(16)	C24	C25	C26	109.2(17)
C19	N14	C17	107.5(16)	C27	C26	C25	111.0(17)
C21	N21	Cu2	111.2(13)	N24	C27	C26	122.4(18)
C23	N22	Cu2	132.9(15)	N24	C27	C28	105.6(17)
C23	N22	C25	116.6(17)	C28	C27	C26	131.8(19)
C25	N22	Cu2	109.9(11)	C27	C28	N23	111.0(19)
C28	N23	Cu1	131.9(15)	N24	C29	N23	112.3(19)

Table S24. Hydrogen bonds for **3.**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O1	H1	O3[1]	0.86(2)	1.93(10)	2.65(3)	141(12)
O2	H2	O13[2]	0.86(2)	2.03(14)	2.651(19)	128(15)
N14	H14	O22[3]	0.88	1.82	2.69(2)	171.1
N24	H24	O12[3]	0.88	1.88	2.76(2)	172.9
N11	H11A	O23[1]	0.91	2.05	2.938(19)	164.8
N21	H21A	O13[2]	0.91	2.15	3.01(2)	157.7

Symmetry code: [1]*1+y,-1+x,-z*; [2]*3-x,2-x+y,1/3-z*; [3]*2-x,1-x+y,1/3-z*

Table S25. Crystal data and structure refinement for **1** at 270 and 370 K.

Crystal Structure	$\mathbf{1_{270}}$	$\mathbf{1_{370}}$
Formula	$[Cu_2(\mathbf{car})_2(H_2O)_2]\cdot 2H_2O$	$[Cu_2(\mathbf{car})_2]\cdot H_2O$
Empirical formula	$C_{18}H_{32}Cu_2N_8O_{10}$	$C_{18}H_{28}Cu_2N_8O_7$
Formula weight	323.80	298.77
Temperature/K	270(1)	370(1)
Crystal system	trigonal	trigonal
Space group	$P3_121$	$P3_121$
a/Å	8.61755(19)	8.3611(10)
b/Å	8.61755(19)	8.3611(10)
c/Å	30.5882(6)	30.450(3)
α/°	90	90
β/°	90	90
γ/°	120	120
Volume/Å³	1967.22(9)	1843.5(5)
Z	3	3
ρ_{calc}g/cm³	1.640	1.604
μ/mm^{-1}	2.593	2.618
F(000)	1002.0	912.0
Crystal size/mm³	0.13 × 0.13 × 0.03	0.13 × 0.13 × 0.03
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.672 to 154.252	12.224 to 152.798
Index ranges	-9 ≤ h ≤ 10 -10 ≤ k ≤ 10 -35 ≤ l ≤ 37	-10 ≤ h ≤ 10 -10 ≤ k ≤ 6 -38 ≤ l ≤ 33
Reflections collected	7754	6498
Independent reflections	2498 [R_{int} = 0.0319, R_{sigma} = 0.0293]	2367 [R_{int} = 0.0661, R_{sigma} = 0.0885]
Data/restraints/param.	2498/38/224	2367/37/209
Goodness-of-fit on F²	1.046	0.963
Final R indexes [I>=2σ (I)]	R_1 = 0.0313, wR_2 = 0.0821	R_1 = 0.0752, wR_2 = 0.1967
Final R indexes [all data]	R_1 = 0.0347, wR_2 = 0.0849	R_1 = 0.1029, wR_2 = 0.2266
Max. diff. peak/hole / e Å^{-3}	0.40/-0.39	0.55/-0.71
Flack parameter	-0.02(2)	0.02(10)

Table S26. Crystal and structure refinement data for **2** at 100K with some sovent oxygen atoms modeled and **2** at 170K refined with the solvent masking routine. Because the solvent atoms were not found in **2**, data connected to the formula could not be calculated.

Crystal structure	$\mathbf{2_{100}}$	$\mathbf{2_{170}}$
Formula	$[Cu_2(\mathbf{car})_2(H_2O)_{0.70}(MeOH)_{0.30}]\cdot mH_2O\cdot nMeOH$	$[Cu_2(\mathbf{car})_2(H_2O)_2]\cdot mH_2O\cdot nMeOH$

Formula weight	-	-
Temperature/K	100(1)	170(1)
Crystal system	orthorhombic	orthorhombic
Space group	*I*222	*I*222
a/Å	12.08961(8)	12.09436(16)
b/Å	20.35323(15)	13.9509(2)
c/Å	13.73806(9)	20.3839(3)
α/°	90	90
β/°	90	90
γ/°	90	90
Volume/Å^3	3380.42(4)	3439.30(8)
Z	4	4
ρ_{calc}g/cm^3	-	-
μ/mm^{-1}	-	-
F(000)	-	-
Crystal size/mm^3	0.061 × 0.046× 0.039	0.155 × 0.148 × 0.098
Radiation	synchrotron (λ = 0.7000)	CuKα (λ = 1.54184)
2Θ range for data collection/°	3.86 to 60	8.502 to 154.736
Index ranges	−17 ≤ h ≤ 17 −27 ≤ k ≤ 27 −19 ≤ l ≤ 19	-14 ≤ h ≤ 15 -17 ≤ k ≤ 17 -20 ≤ l ≤ 25
Reflections collected	29910	10171
Independent reflections	4990 [R_{int} = 0.0370, R_{sigma} = 0.0157]	3440 [R_{int} = 0.0150, R_{sigma} = 0.0128]
Data/restraints/param.	4990/10/185	3440/0/166
Goodness-of-fit on F^2	1.047	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0296, wR_2 = 0.0805	R_1 = 0.0298, wR_2 = 0.0816
Final R indexes [all data]	R_1 = 0.0296, wR_2 = 0.0805	R_1 = 0.0299, wR_2 = 0.0818
Max. diff. peak/hole / e Å^{-3}	0.43/-0.37	0.60/-0.32
Flack parameter	0.024(5)	0.026(9)

Table S27. Crystal and structure refinement data for **3** at 150K.

Crystal structure	**3**
Formula	$[Cu_2(\mathbf{car})_2(MeOH)_2]\cdot 5.5$ MeOH
Empirical formula	$C_{25.5}H_{54}Cu_2N_8O_{13.5}$
Formula weight	815.84
Temperature/K	150(1)
Crystal system	trigonal
Space group	$P3_121$
a/Å	13.3717(9)
b/Å	13.3717(9)
c/Å	36.410(2)

α/°	90
β/°	90
γ/°	120
Volume/Å^3	5637.9(6)
Z	6
ρ_{calc}g/cm^3	1.442
μ/mm^{-1}	1.201
F(000)	2574.0
Crystal size/mm^3	0.44 × 0.25 × 0.20
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	8.59 to 49.76
Index ranges	$-14 \le h \le 14$, $-15 \le k \le 15$, $-42 \le l \le 42$
Reflections collected	13784
Independent reflections	14149 [R_{int} = 0.096]
Data/restraints/param.	13784/49/306
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.1068, wR_2 = 0.1967
Final R indexes [all data]	R_1 = 0.1463, wR_2 = 0.2223
Max. diff. peak/hole / e Å^{-3}	1.11/−1.02
Flack parameter	0.022(19)