

## Electronic Supplementary Information

# Hydrophobic-exterior layer structures and magnetic properties of trinuclear copper complexes with chiral amino alcoholate ligands

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Figure S18

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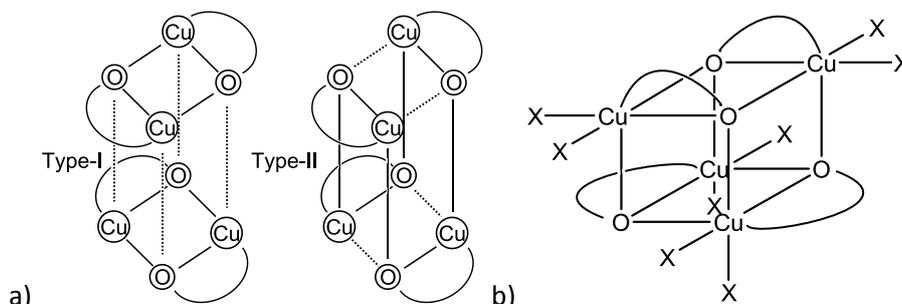
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Packing diagrams for compound **9** (Fig. S19 and S20)

Comment on X-ray refinement special details for compound **9**

### Further introduction to copper-amino alcoholate complexes:

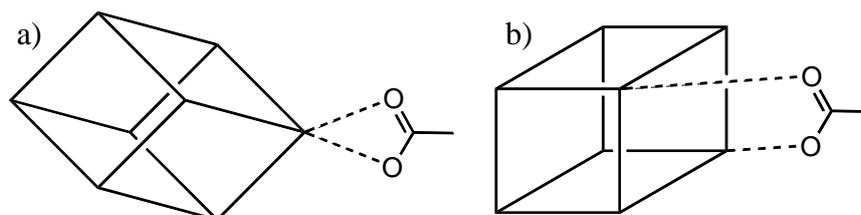
Amino alcoholate ligands can also yield two different types of  $\text{Cu}_4\text{O}_4$  hetero-cubanes (Scheme S1Scheme).<sup>1-9</sup> Type I consists of two pseudo-dimeric units with four short Cu-O distances, which are connected via four long Cu-O distances, while type II is an open- or pseudo-cubane structure there the short distances between the  $\text{Cu}_4\text{O}_4$  atoms give an eight-membered ring (Scheme S1a). Various intermediate forms exist including a rather regular  $\text{Cu}_4\text{O}_4$  hetero-cubane with all Cu-O distances being very similar. These geometric differences depend on the substituents on the amino alcoholate and the halogen or pseudohalogen ligands (marked as X in Scheme S1b).<sup>10-12</sup>



**Scheme S1** a) Two different types of  $\text{Cu}_4\text{O}_4$ -heterocubane cores built up from Cu(II) and amino alcoholates; b) schematic cubane-type SBU with octahedral coordination sphere of Cu-cations. Structures exist for X = Cl, Br, I,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , malonate, triflate, octacyanomellates (IV).

The coordination sites marked with an X in Scheme S1 can be occupied (both or only one per Cu atom) by different anions such as chloride<sup>13</sup> nitrate<sup>14</sup>, bromide<sup>15</sup>, malonate<sup>16</sup> and sulphate.<sup>17</sup> Due to the different ways to coordinate the Cu cations, many different networks would be possible if these ligands were bridging ligands. When octacyanomellates(IV) were used, some 3D cluster arrays of metal-organic frameworks were reported.<sup>18</sup>

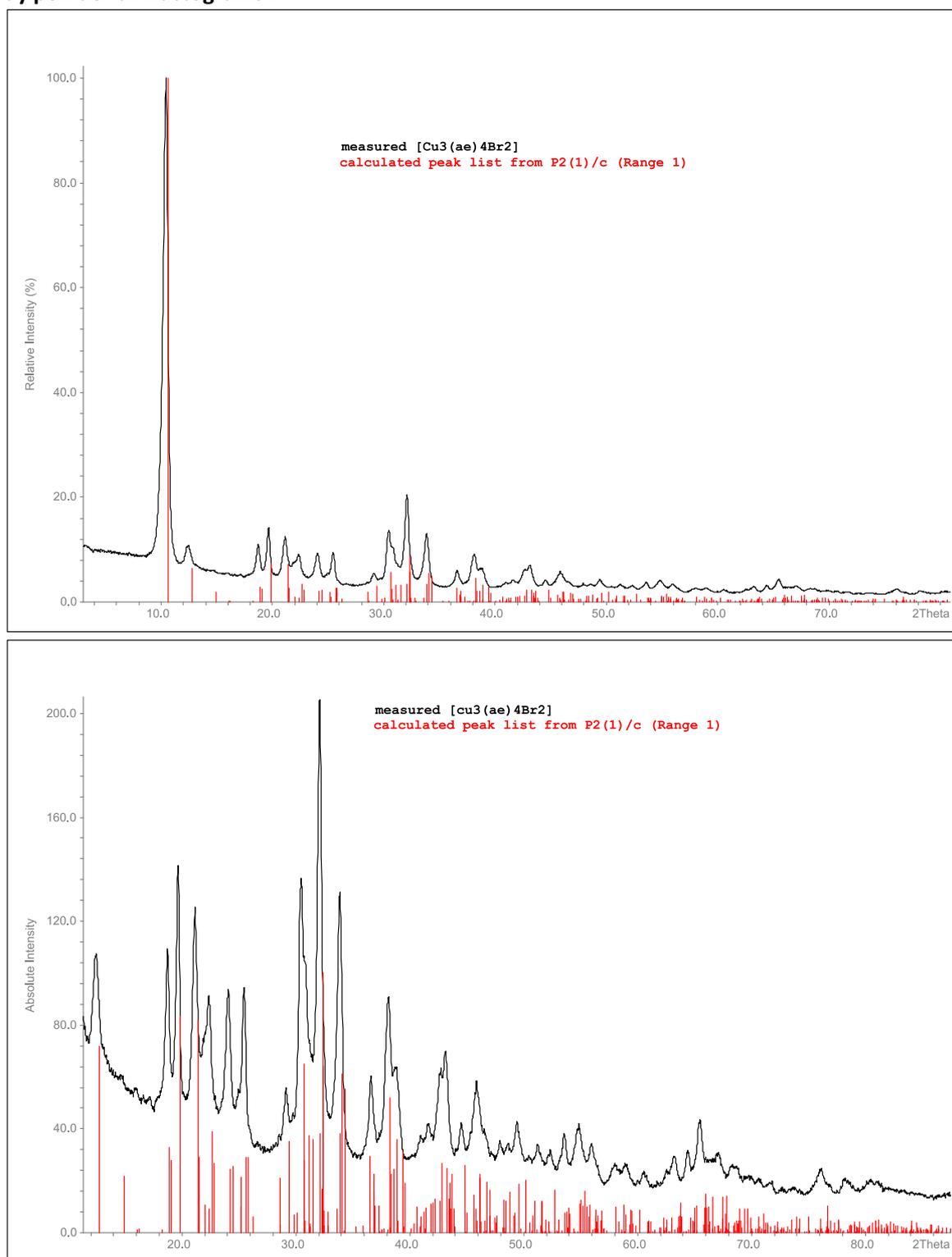
In other cases, anions of acids were used to coordinate to the cubane-like core, occupying both coordination sites. The carboxylate groups either chelate one corner atom<sup>19</sup> (Scheme S2a) or diagonally bridge two copper cations<sup>8, 20-24</sup> (Scheme S2b), in each case facing tetrahedrally away from the cubane-like core. If these acids would be exchanged with bridging acids such as terephthalic acid, very interesting diamond-like topographies could be obtained.



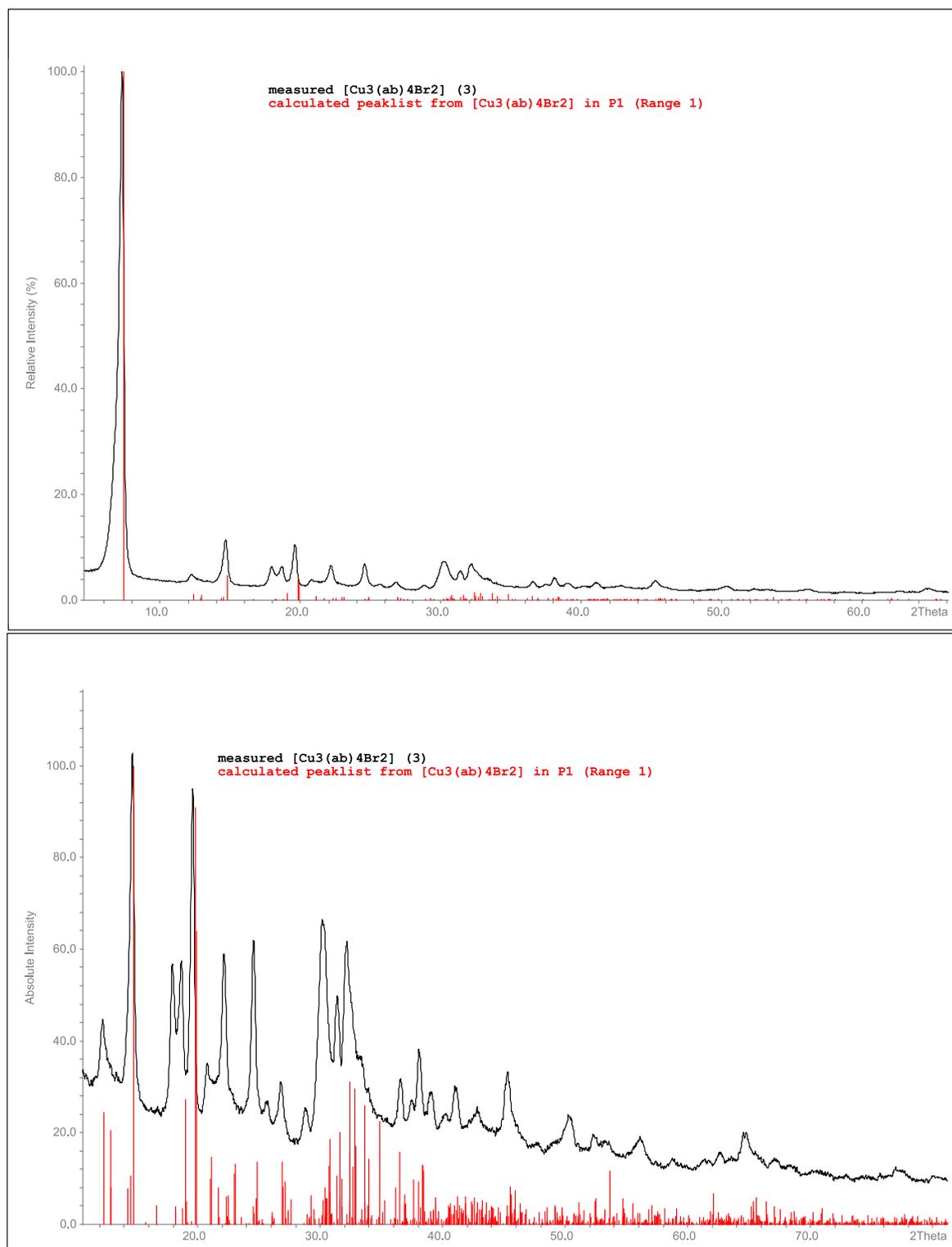
**Scheme S2** The carboxylate groups either chelate one corner atom<sup>19</sup> (a) or diagonally bridge two copper cations<sup>8, 20-24</sup> (b).

Some of the reported cubane-type compounds have been used as starting materials for mixed metal compounds and extended clusters.<sup>2, 25</sup> Two synthetic approaches are possible to obtain the desired new compounds containing the cubanes as SBUs connected by bridging ligands. One is by synthesising one of the reported compounds with subsequent substitution of an anionic ligand with a bridging ligand; the other is to follow a similar synthesis to that reported already adding the bridging ligands into the reaction mixture. In this work, both possibilities were undertaken with different coordinating bridging anions, weakly coordinating anions, and the same anions used in the structures reported above. Also copper salts with weakly coordinating anions (such as  $\text{BF}_4$ ,  $\text{ClO}_4$  and  $\text{PF}_6$ ) in combination with different chiral amino alcohols were directly mixed with the acids of bridging dicarboxylate ligands such as benzene-1,4-dicarboxylate ( $\text{bdc}^{2-}$ ), benzene-1,4-dicarboxylate ( $\text{ip}^{2-}$ ) or (as uncharged bridging ligands) 4,4'-bipyridine (4,4'-bipy) and 1,2-bis(1,2,4-triazol-4-yl)ethane (btre).

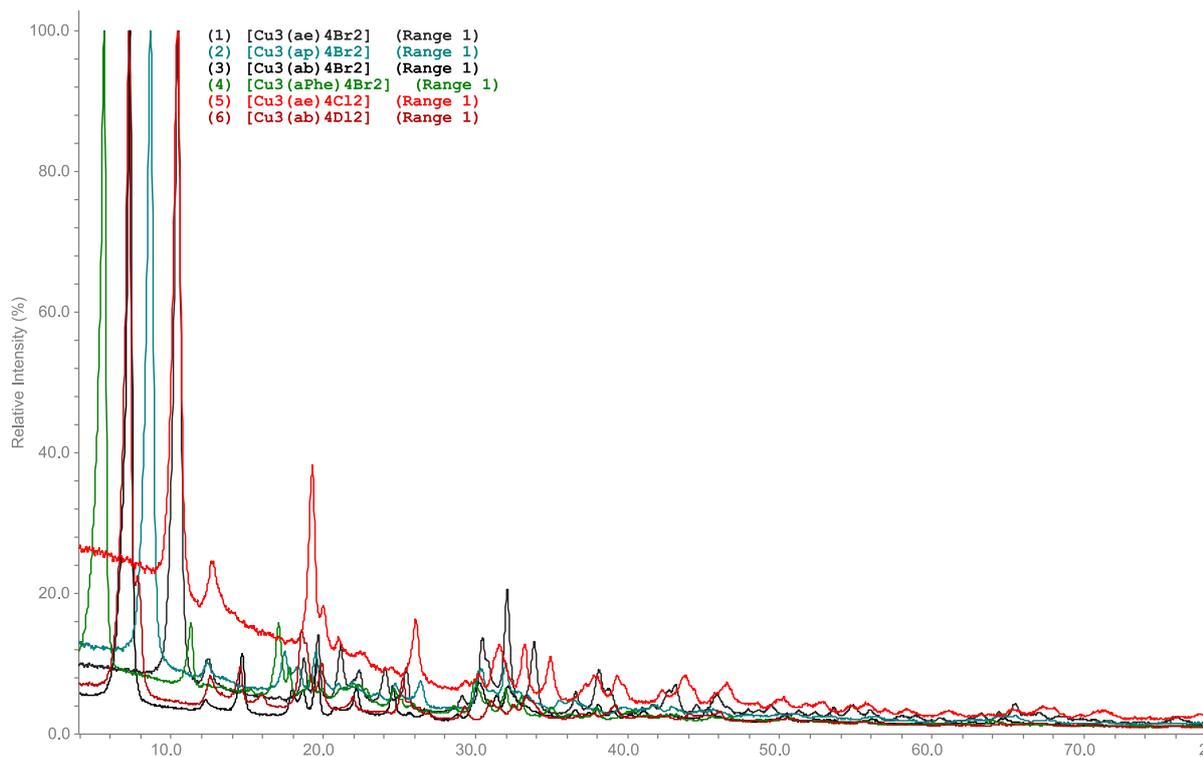
### X-ray powder diffractograms :



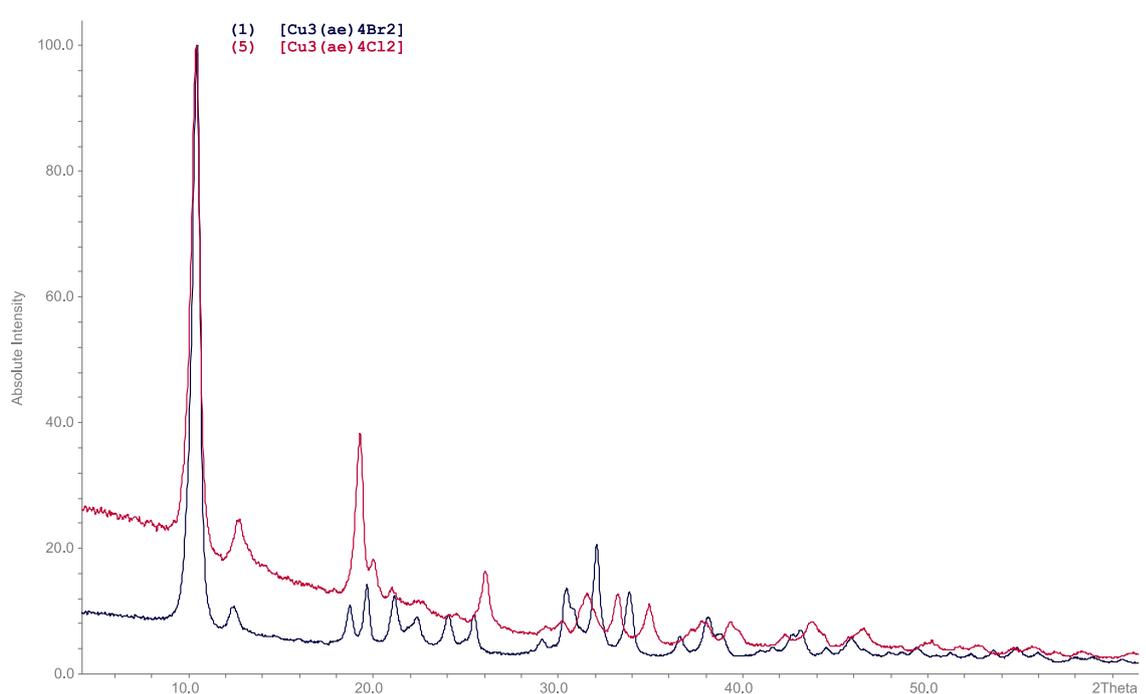
**Fig. S1** Powder diffractogram of compound **1**; experimental in black; theoretical pattern calculated from the single crystal data in red. (a) Diffractogram from  $2\theta = 3-80^\circ$ ; (b) Diffractogram from  $11-88^\circ$ .



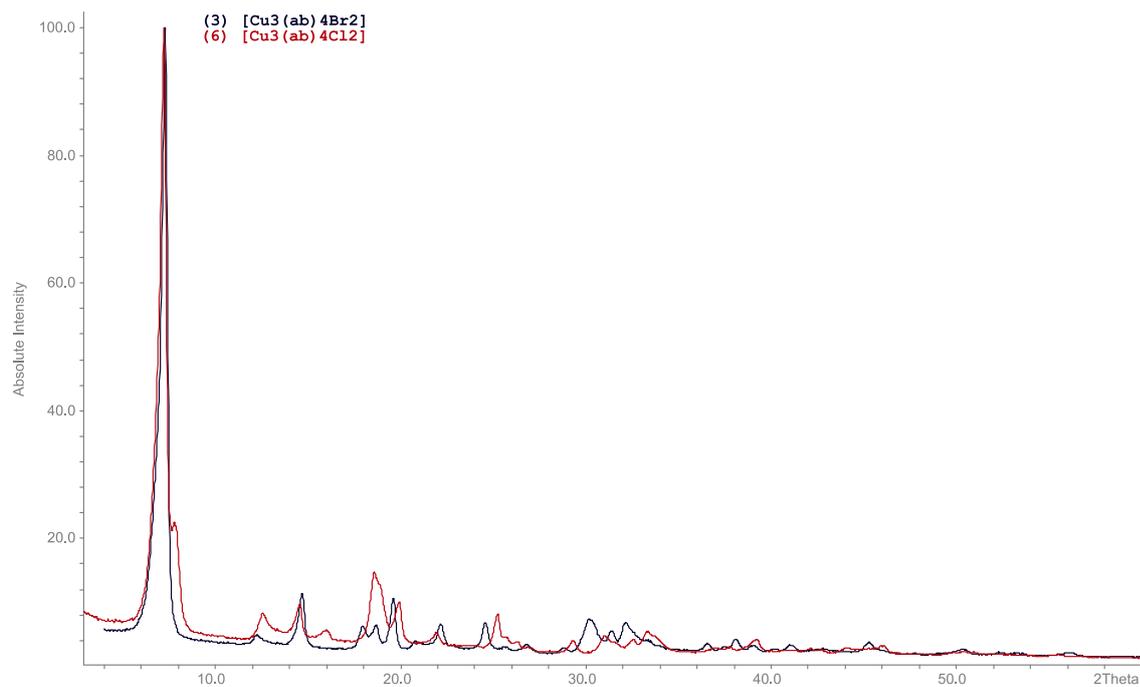
**Fig. S2** Powder diffraction of compound **3**; experimental in black; theoretical pattern calculated from the single crystal data in red. (a) Diffraction from  $2\theta = 5-66^\circ$ ; (b) Diffraction from  $11-80^\circ$ .



**Fig. S3** Combination of the powder diffractograms of compound **1-6**, with the different interlayer spacing clearly visible between  $2\theta = 4-11^\circ$ .



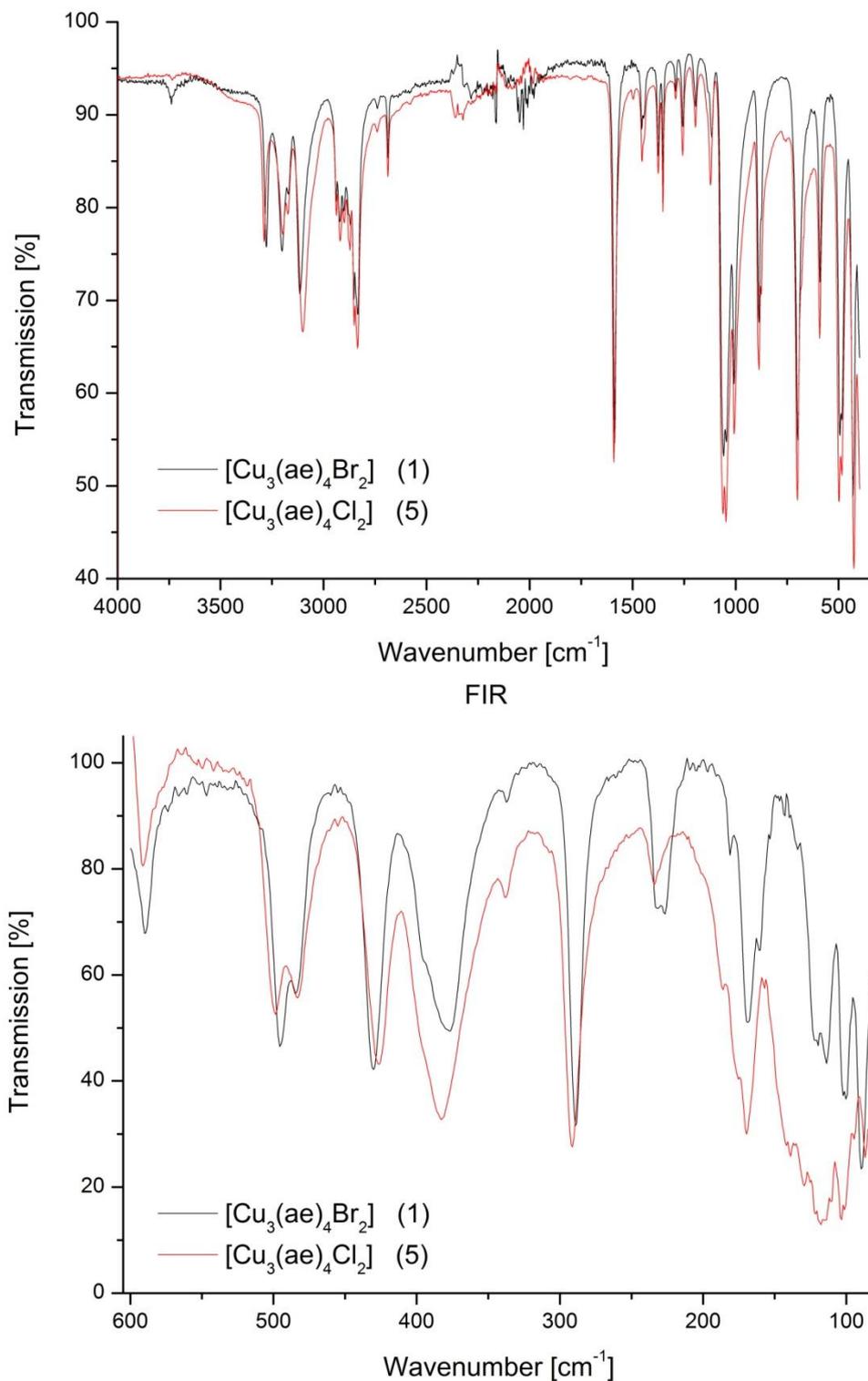
**Fig. S4** Powder diffractograms of compound **1** (black) and of compound **5** (red) with the same amino ethanolate (ae) but different halide ligands (Br in **1**, Cl in **5**). Clearly visible the same interlayer spacing and structural similarity with slight shifts due to the different size of the halide ligands (e.g. the two peaks at  $2\theta = 18.7^\circ$  and  $19.6^\circ$  merge to one peak at  $19.2^\circ$ ).



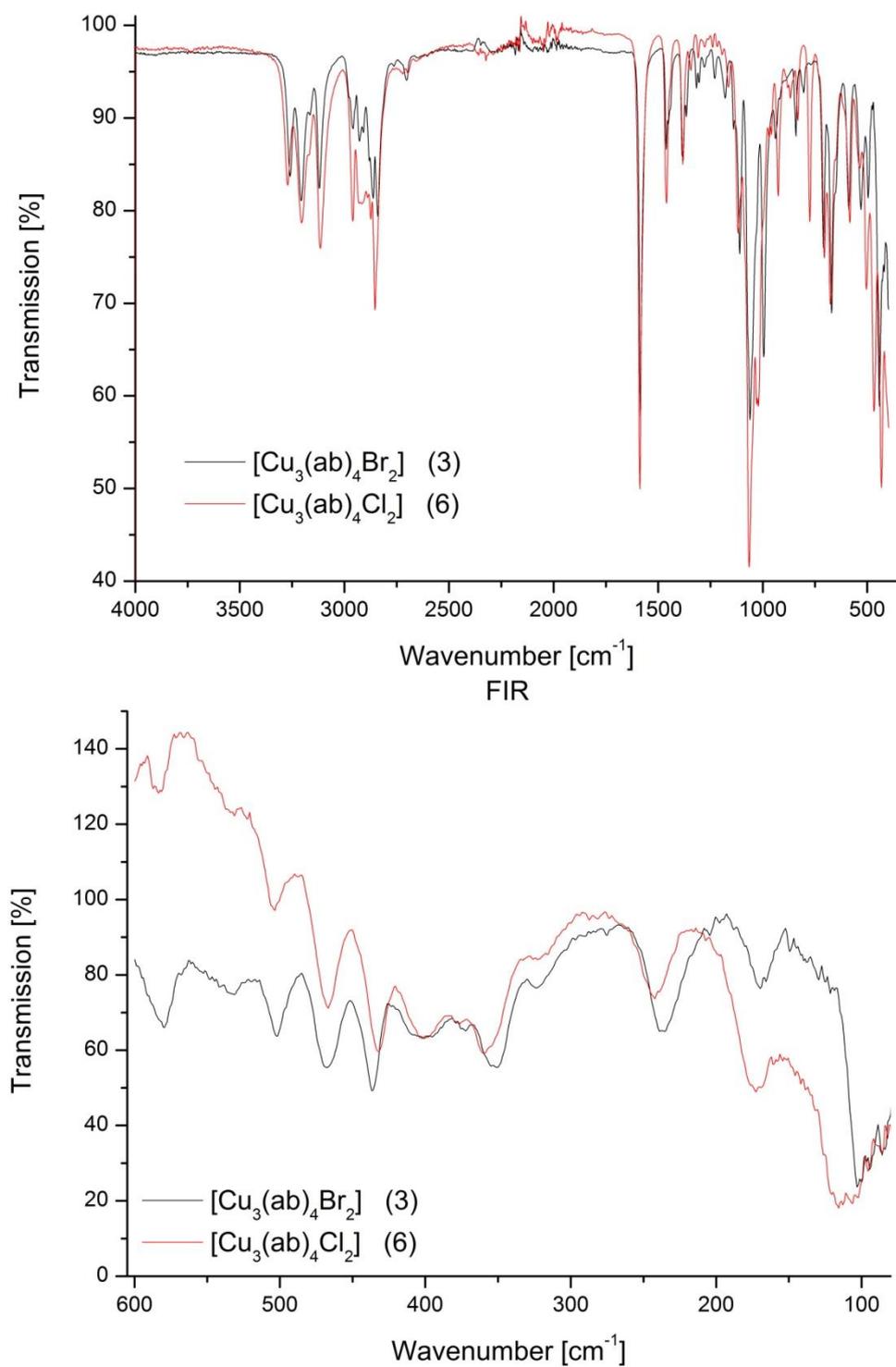
**Fig. S5** Powder diffractograms of compound **3** (black) and of compound **6** (red) with the same (*R*)-2-amino-butan-1-olate (ab) but different halide ligands (Br in **3**, Cl in **6**). Clearly visible the same interlayer spacing and structural similarity with slight shifts due to the different size of the halide ligands.

### Infrared spectra:

MIR and FIR of compound **1** and **3** in direct comparison with compound **5** and **6**, respectively.

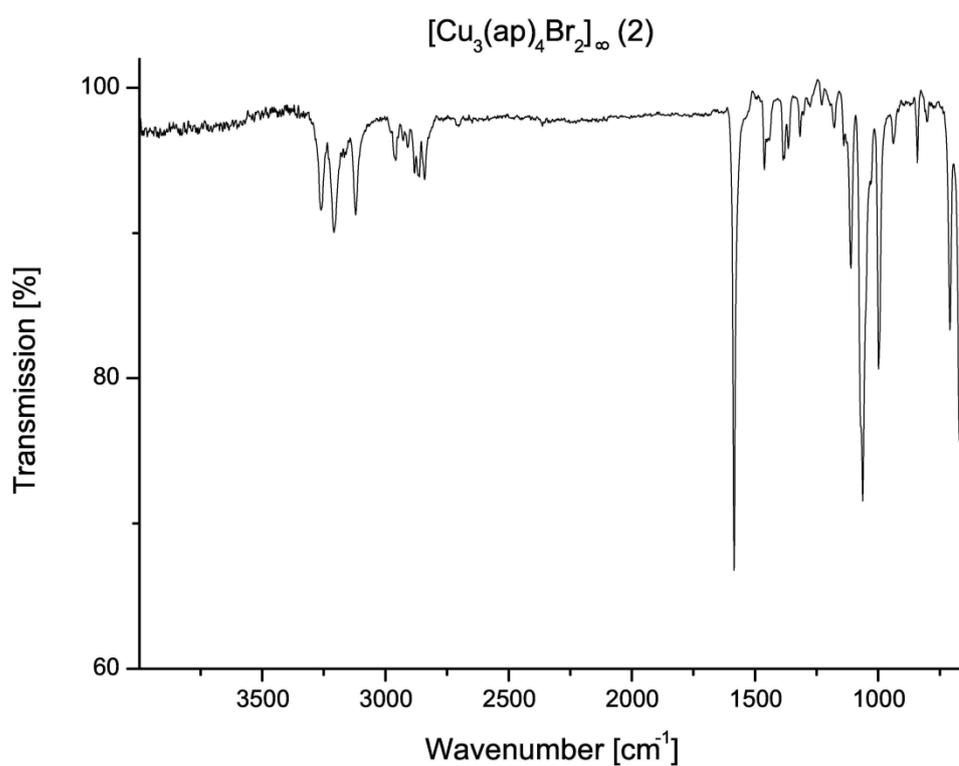
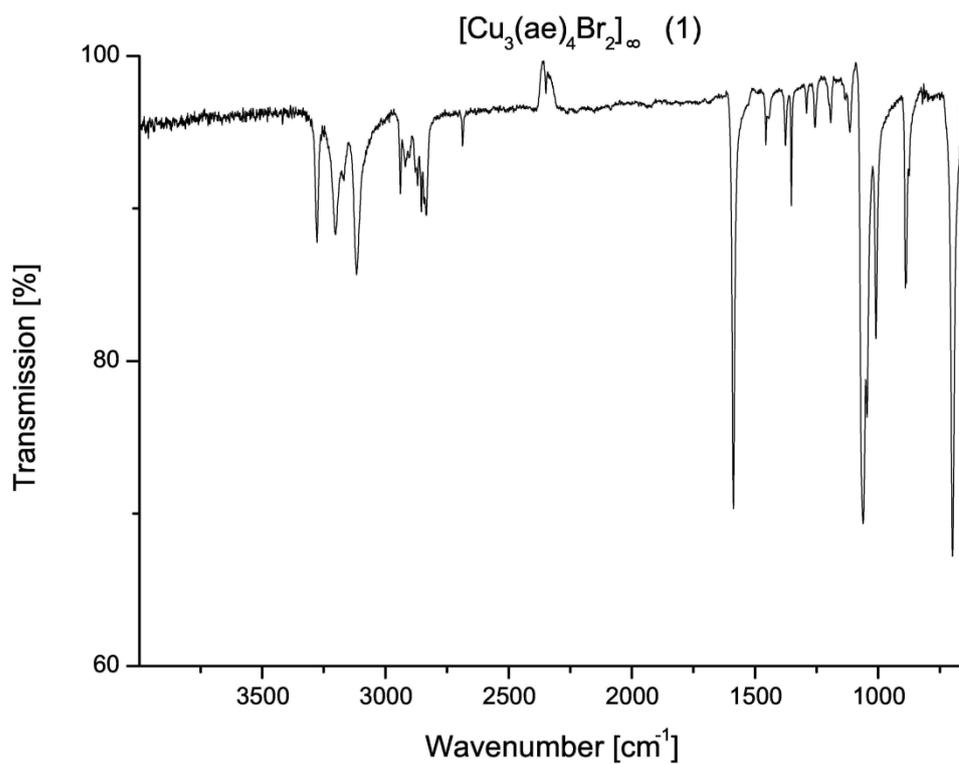


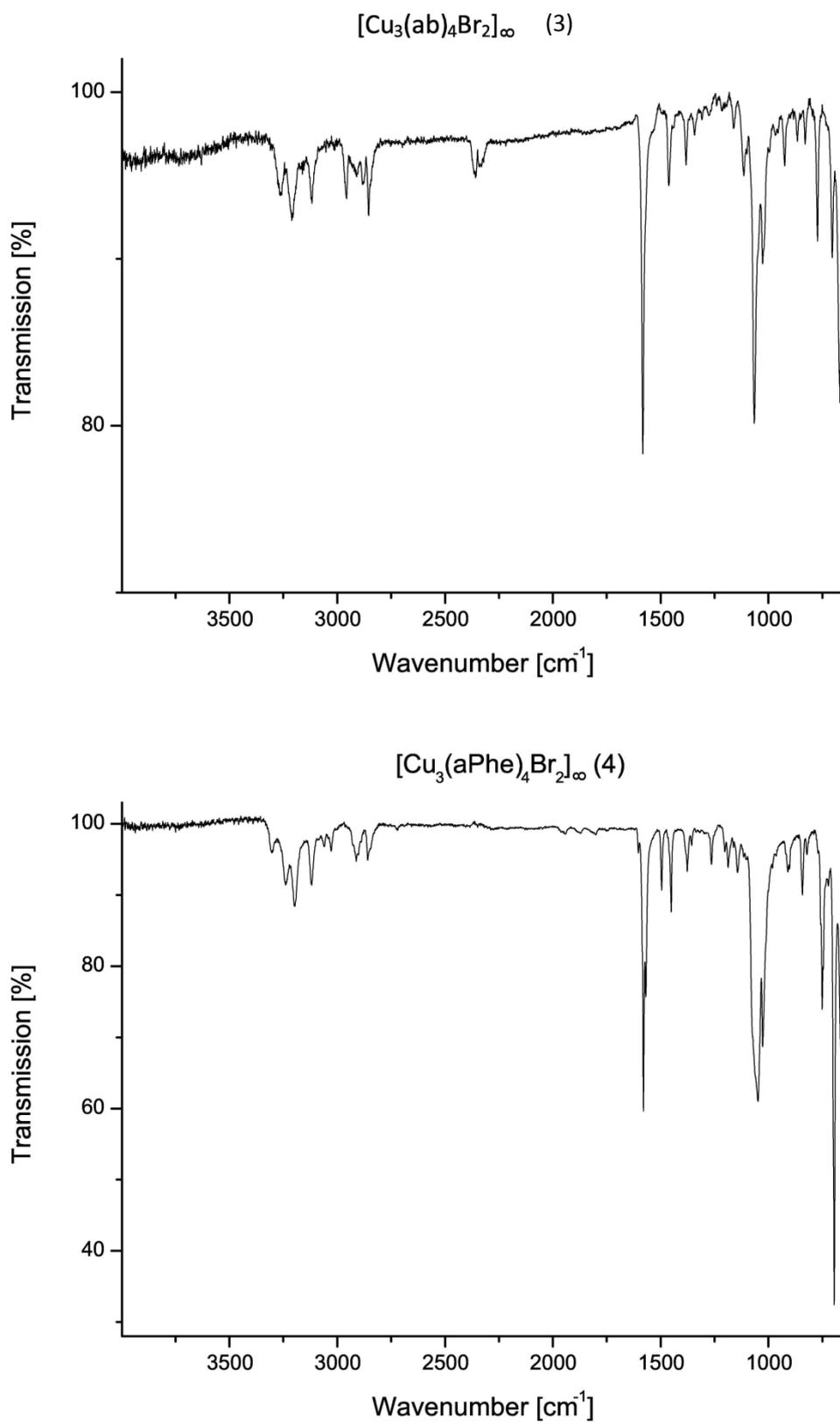
**Fig. S6** (a) Medium IR (MIR) and (b) Far IR (FIR) spectra of compound **1** (black curve) and **5** (red curve) with the same amino ethanolate (ae) but different halide ligands (Br in **1**, Cl in **5**) for comparison.



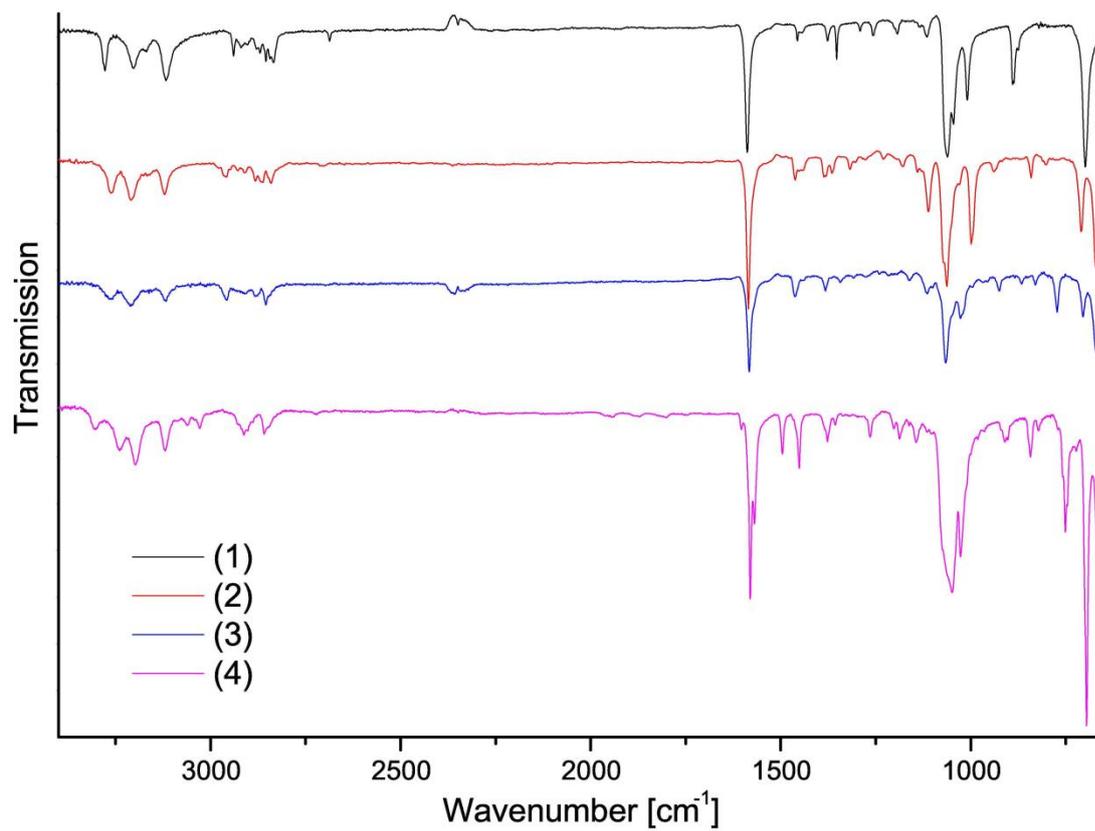
**Fig. S7** (a) Medium IR (MIR) and (b) Far IR (FIR) spectra of compound **3** (black curve) and **6** (red curve) with the same (*R*)-2-amino-butan-1-olate (ab) but different halide ligands (Br in **3**, Cl in **6**) for comparison

MIR spectra of compounds **1**, **2**, **3** and **4**:





**Fig. S8** Medium IR (MIR) spectra of compounds **1**, **2**, **3** and **4**.

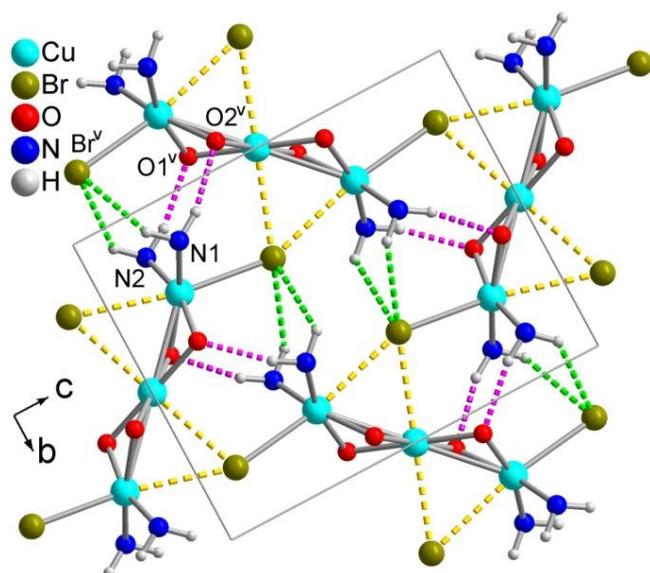


**Fig. S9** Overlay of medium IR (MIR) spectra of compounds **1**, **2**, **3** and **4**.

**Table S1** Hydrogen-bond lengths (Å) and angles (°) in **1** and **3**.<sup>a</sup>

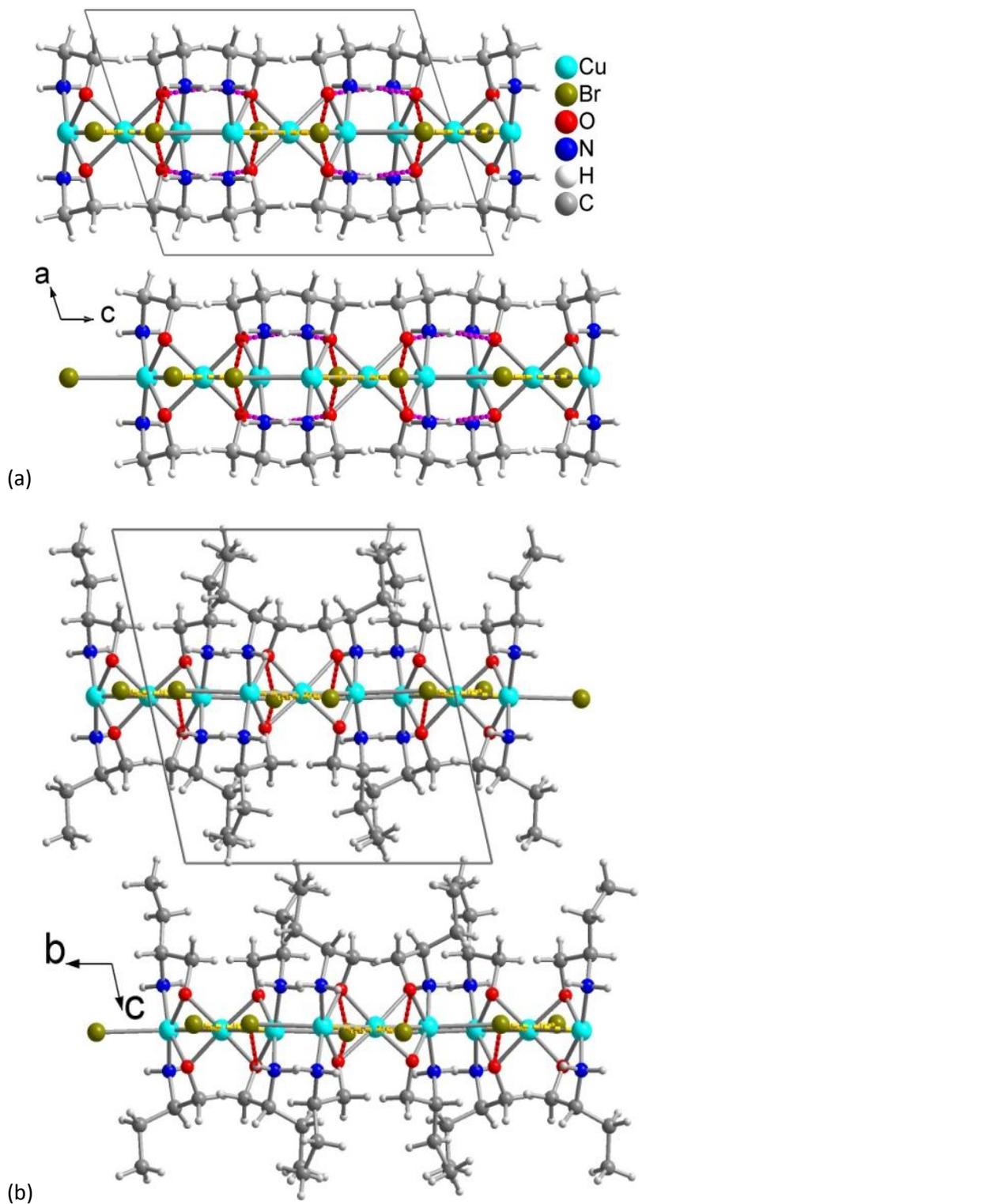
		N-H	H...O/Br	N...O/Br	N-H...O/Br	symm operation
<b>1</b>	N1-H1A...O2 <sup>v</sup>	0.92	2.09	2.997(4)	167	$v = x+1, y-0.5, -z+0.5$
	N2-H2B...O1 <sup>v</sup>	0.92	2.06	2.963(4)	166	$v = x+1, y-0.5, -z+0.5$
	N1-H1B...Br <sup>v</sup>	0.92	2.80	3.455(4)	129	$v = x+1, y-0.5, -z+0.5$
	N2-H2A...Br <sup>v</sup>	0.92	2.74	3.414(4)	131	$v = x+1, y-0.5, -z+0.5$
<b>3</b>	N1-H1A...Br3	0.92	2.92	3.52(2)	124	
	N1-H1B...O6	0.92	2.22	3.13(3)	169	
	N2-H2A...O5	0.92	2.17	3.07(2)	164	
	N2-H2B...Br3	0.92	2.75	3.463(18)	135	
	N3-H3A...Br4 <sup>vi</sup>	0.92	2.91	3.517(17)	125	$vi = x+1, y-1, z$
	N3-H3B...O8 <sup>vi</sup>	0.92	2.19	3.10(2)	168	$vi = x+1, y-1, z$
	N4-H4A...O7 <sup>vi</sup>	0.92	2.14	3.03(3)	164	$vi = x+1, y-1, z$
	N4-H4B...Br4 <sup>vi</sup>	0.92	2.71	3.44(2)	137	$vi = x+1, y-1, z$
	N5-H5A...Br1 <sup>ix</sup>	0.92	2.91	3.544(16)	128	$vii = x-1, y, z$
	N5-H5B...O2 <sup>vii</sup>	0.92	2.21	3.10(3)	164	$vii = x-1, y, z$
	N6-H6A...O1 <sup>vii</sup>	0.92	2.11	3.00(3)	162	$vii = x-1, y, z$
	N6-H6B...Br1 <sup>vii</sup>	0.92	2.70	3.43(2)	137	$vii = x-1, y, z$
	N7-H7A...Br2 <sup>viii</sup>	0.92	2.88	3.500(18)	126	$viii = x-1, y+1, z$
	N7-H7B...O4 <sup>viii</sup>	0.92	2.21	3.11(3)	168	$viii = x-1, y+1, z$
	N8-H8B...Br2 <sup>viii</sup>	0.92	2.73	3.458(17)	137	$viii = x-1, y+1, z$
	N8-H8B...O3 <sup>viii</sup>	0.92	2.14	3.03(2)	162	$viii = x-1, y+1, z$

<sup>a</sup> For found and refined atoms the standard deviations are given. For atom labels, see Fig. 3b or Fig. S10.



**Fig. S10** (= Fig. 3b, repeated here to accompany Table S1) 2D-layer in **1** (and similar in **3**) with charge-assisted Cu<sup>(2+)</sup>...<sup>(-)</sup>Br contacts depicted as dotted yellow lines and additional charge-assisted N-H...<sup>(-)</sup>O (pink) and N-H...<sup>(-)</sup>Br (green) hydrogen bonds (C-atoms are omitted for clarity). H-bond distances and angles in Table S1 in ESI<sup>†</sup>. Symmetry transformation  $v = x+1, y-0.5, -z+0.5$ .

Packing diagrams of **1** and **3**:



**Fig. S11** Packing diagram of (a) **1** and (b) **3** with Cu<sup>(2+)</sup>...<sup>(-)</sup>Br contacts as yellow dashed lines and N-H...<sup>(-)</sup>O and N-H...<sup>(-)</sup>Br hydrogen bonds indicated as red dashed lines.

### Comment on X-ray refinement special details for compound 3

48 Uiso/Uij restrained atom sites, 48 distance or angle restraints and 549 least-squares restraints were used in the refinement of compound 3.

Due to the twining, the crystal morphology and the missing absorption correction during data reduction (discussed in paper) the anisotropic displacement parameter of the light atoms were "smeared out" and unrealistic.

The restraints SIMU (similar  $U_{ij}$  values for adjoining atoms) and DELU (rigid-bond) were applied to the  $U_{ij}$  values of all N, C and O atoms with the default esd. (SIMU \$N \$C \$O, DELU \$N \$O \$C). However, some atoms went to non-positive-definite and were further restrained with a soft restraint to be approximately isotropic with the ISOR restraint with default esd. (ISOR O1 O3 O5 O7 N2 N5 N7 C13 C14 C17 C21)

The eight chemically equivalent but crystallographically independent alcoholate ligands were restrained to have similar geometries to one another without limiting torsion angles with a combination of SADI restraints.

SADI O1 C1 O2 C5 O3 C9 O4 C13 O5 C17 O6 C21 O7 C25 O8 C29

SADI C1 C2 C5 C6 C9 C10 C13 C14 C17 C18 C21 C22 C25 C26 C29 C30

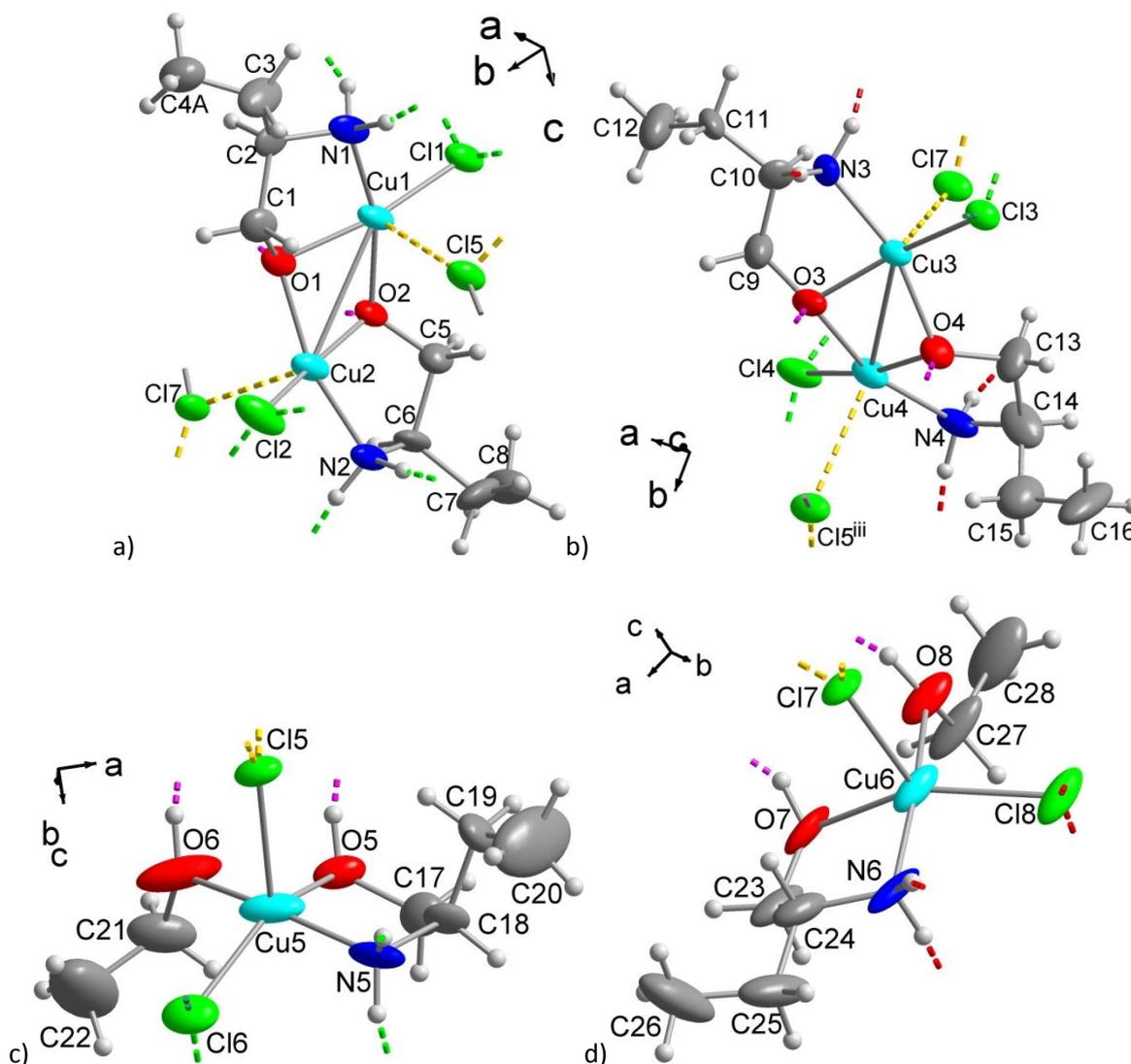
SADI N1 C2 N2 C6 N3 C10 N4 C14 N5 C18 N6 C22 N7 C26 N8 C30

SADI C2 C3 C6 C7 C10 C11 C14 C15 C18 C19 C22 C23 C26 C27 C30 C31

SADI C3 C4 C7 C8 C11 C12 C15 C16 C19 C20 C23 C24 C27 C28 C31 C32

## 1D coordination polymers with mono and dinuclear SBUs: Compounds 7 and 8

Dinuclear and mononuclear SBUs of compound 8



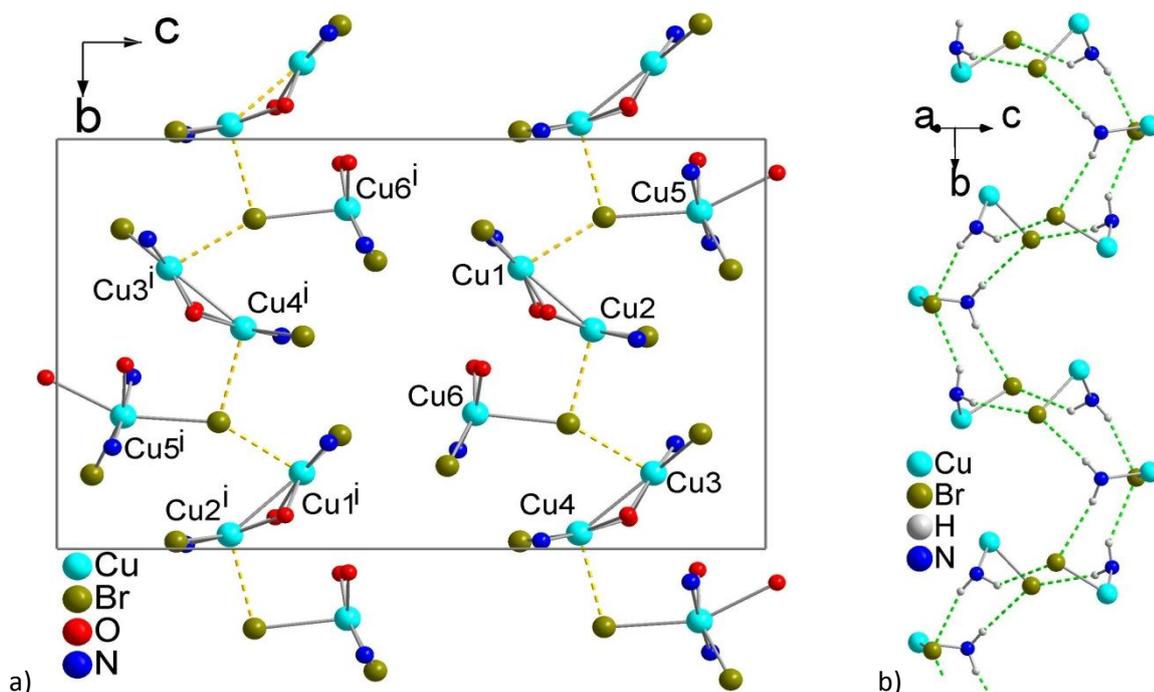
**Fig. S12** (a) and (b) Dinuclear and (c), (d) mononuclear SBUs of compound **8** (50% thermal ellipsoids); charge-assisted Cu<sup>(2+)</sup>...<sup>(-)</sup>Br (dashed yellow lines), N-H...<sup>(-)</sup>O (pink) and N-H...<sup>(-)</sup>Br (green) contacts are indicated; symmetry operation iii = x, 1+y, z; disorder of ethyl groups are not shown for clarity; distances and angles in Table S2.

All ethyl groups of the amino alcohol ligand are disordered and have two orientations, due to rotation around the bond between the asymmetric C-atom (C2, C6, C10, C14, C18, C24) and the ethyl-CH<sub>2</sub>-carbon atom.

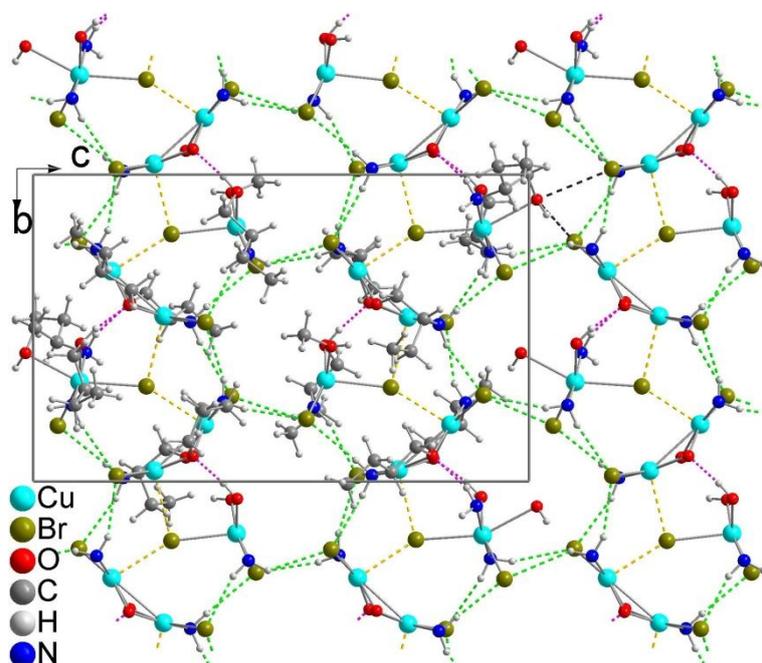
**Table S2** Selected bond lengths and angles of the SBUs of compound **7** and **8**

<b>7</b>				<b>8</b>			
Bond lengths / Å		Angles / °		bond lengths / Å		Angles / °	
dinuclear SBU							
Cu1-O1	1.99(2)	O1-Cu1-O2	79.8(10)	Cu1-O1	1.983(7)	O1-Cu1-O2	78.2(3)
Cu1-O2	1.93(2)	O1-Cu1-N1	83.5(10)	Cu1-O2	1.949(7)	O1-Cu1-N1	84.8(3)
Cu1-N1	1.89(2)	O1-Cu1-Br1	163.9(7)	Cu1-N1	1.961(9)	O1-Cu1-Cl1	163.5(2)
Cu1-Br1	2.362(5)	Br1-Cu1-Br5	97.75(18)	Cu1-Cl1	2.249(3)	Cl1-Cu1-Cl5	101.3(1)
Cu1-Br5	2.894(5)	Cu1-O1-Cu2	91.6(10)	Cu1-Cl5	2.781(3)	Cu1-O1-Cu2	94.7(3)
Cu1-Cu2	2.869(6)	Cu1-O2-Cu2	93.0(10)	Cu1-Cu2	2.8982(18)	Cu1-O2-Cu2	95.1(3)
Cu2-O1	2.02(2)	O1-Cu2-O2	76.8(9)	Cu2-O1	1.957(7)	O1-Cu2-O2	78.2(3)
Cu2-O2	2.02(2)	O2-Cu2-N2	85.1(10)	Cu2-O2	1.978(7)	O2-Cu2-N2	84.8(3)
Cu2-N2	2.01(2)	O2-Cu2-Br2	169.4(6)	Cu2-N2	1.967(9)	O2-Cu2-Cl2	166.6(2)
Cu2-Br2	2.375(6)	Br2-Cu2-Br7	94.0(1)	Cu2-Cl2	2.244(3)	Cl2-Cu2-Cl7	98.3(1)
Cu2-Br7	3.019(4)			Cu2-Cl7	2.789(3)		
dinuclear SBU							
Cu3-O3	2.012(17)	O3-Cu3-O4	76.5(8)	Cu3-O3	1.984(7)	O3-Cu3-O4	78.7(3)
Cu3-O4	1.92(2)	O3-Cu3-N3	86.4(8)	Cu3-O4	1.977(7)	O3-Cu3-N3	83.7(3)
Cu3-N3	1.97(2)	O3-Cu3-Br3	163.5(5)	Cu3-N3	1.961(8)	O3-Cu3-Cl3	164.4(2)
Cu3-Br3	2.398(4)	Br3-Cu3-Br7	102.9(1)	Cu3-Cl3	2.236(3)	Cl3-Cu3-Cl7	97.7(1)
Cu3-Br7	2.921(4)	Cu3-O3-Cu4	93.1(7)	Cu3-Cl7	2.772(3)	Cu3-O3-Cu4	94.9(3)
Cu3-Cu4	2.857(5)	Cu3-O4-Cu4	94.9(9)	Cu3-Cu4	2.9108(18)	Cu3-O4-Cu4	95.1(3)
Cu4-O3	1.923(19)	O3-Cu4-O4	77.6(8)	Cu4-O3	1.966(6)	O3-Cu4-O4	79.3(3)
Cu4-O4	1.960(18)	O4-Cu4-N4	86.3(9)	Cu4-O4	1.969(7)	O4-Cu4-N4	83.8(3)
Cu4-N4	1.93(2)	O3-Cu4-Br4	98.0(5)	Cu4-N4	1.964(9)	O3-Cu4-Cl4	96.4(2)
Cu4-Br4	2.394(5)	Br4-Cu4-Br <sup>iii</sup>	96.8(1)	Cu4-Cl4	2.247(3)	Cl4-Cu1-Cl5 <sup>iii</sup>	95.2(1)
Cu4-Br5 <sup>iii</sup>	3.028(4)			Cu4-Cl5 <sup>iii</sup>	2.863(3)		
mononuclear SBU							
Cu5-N6	1.97(2)	N5-Cu5-N6	173.0(11)				
Cu5-O5	2.067(18)	O5-Cu5-N5	82.9(9)	Cu5-O5	2.051(12)	O5-Cu5-O6	77.5(5)
Cu5-O6	2.564(18)	N6-Cu5-O5	90.6(9)	Cu5-O6	1.993(10)	O5-Cu5-N5	90.6(5)
Cu5-N5	1.87(2)	O5-Cu5-Br6	159.6(6)	Cu5-N5	1.967(10)	O6-Cu5-N5	164.8(4)
Cu5-Br5	2.776(5)	N5-Cu5-Br5	96.7(7)	Cu5-Cl5	2.510(3)	N5-Cu5-Cl6	91.8(3)
Cu5-Br6	2.454(5)	Br5-Cu5-Br6	109.02(17)	Cu5-Cl6	2.269(4)	Cl5-Cu5-Cl6	112.44(11)
mononuclear SBU							
Cu6-O7	2.11(2)	O7-Cu6-O8	89.8(12)	Cu6-O7	2.082(8)	O7-Cu6-O8	88.2(3)
Cu6-O8	1.91(3)	O7-Cu6-N7	78.8(11)	Cu6-O8	1.979(8)	O7-Cu6-N6	81.8(4)
Cu6-N7	2.00(3)	O8-Cu6-N7	166.0(12)	Cu6-N6	1.963(11)	O8-Cu6-N6	168.6(4)
Cu6-Br7	2.727(5)	O7-Cu6-Br8	159.0(9)	Cu6-Cl7	2.483(3)	N7-Cu6-Cl8	149.2(2)
Cu6-Br8	2.394(6)	Br7-Cu6-Br8	107.9(2)	Cu6-Cl8	2.281(4)	Cl7-Cu6-Cl8	114.16(11)

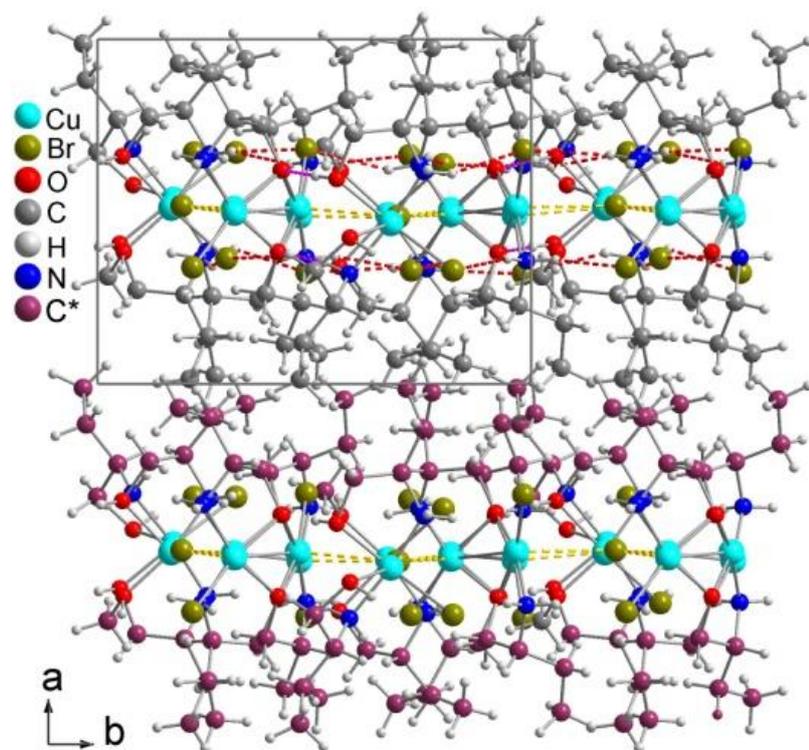
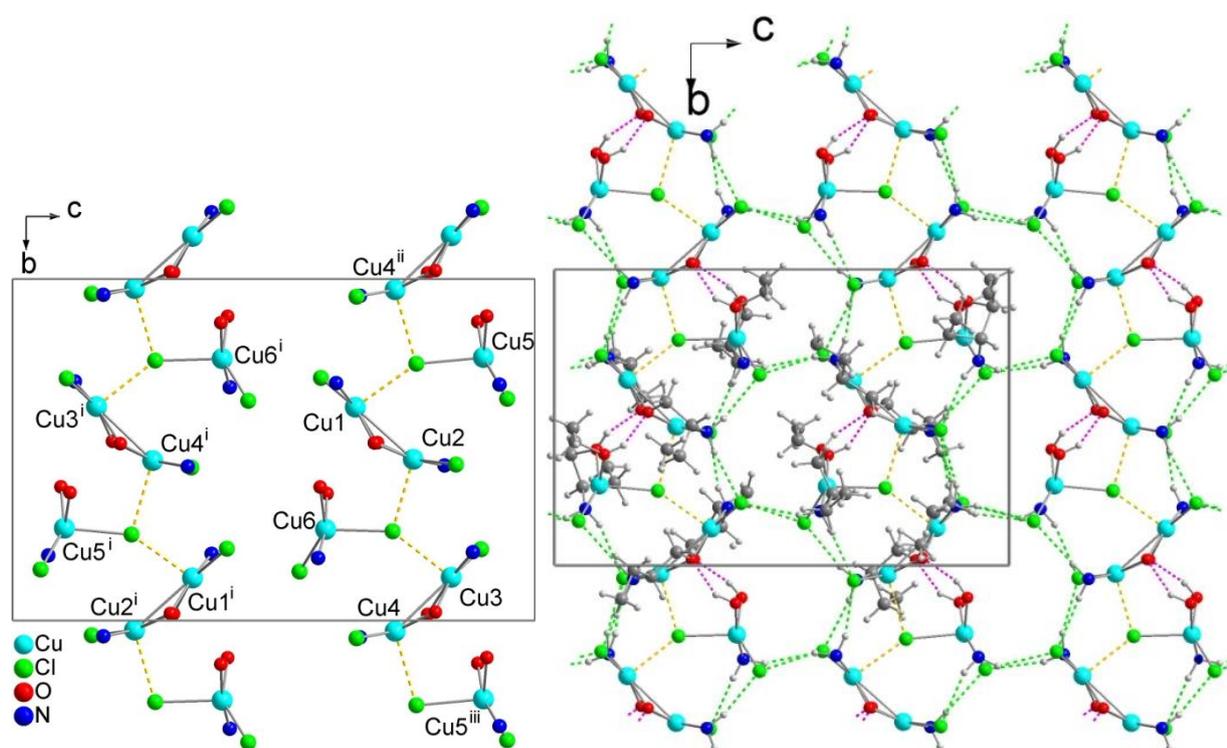
Supramolecular 2D-layer and H-bonding networks in **7** and **8**:



**Fig. S13** a) 1D strands in **7** through charge-assisted  $\text{Cu}^{(2+)}\dots^{(-)}\text{Br}$  interactions (yellow dotted lines); C and H atoms are not shown for clarity; symmetry transformation  $i = 1-x, -0.5+y, 1-z$   
b) The parallel running  $\text{N-H}\dots^{(-)}\text{Br}$  bonds (green) which connects the two strands. For clarity, only the atoms taking part in the H-bond network and the Cu atoms within the two parallel running strands are shown.



**Fig. S14** Supramolecular 2D-layer of compound **7**. C and H atoms are only shown on two asymmetric units, and are omitted on the rest of the network for better visibility of the supramolecular charge-assisted  $\text{Cu}^{(2+)}\dots^{(-)}\text{Br}$  (dashed yellow lines),  $\text{N-H}\dots^{(-)}\text{O}$  (pink) and  $\text{N-H}\dots^{(-)}\text{Br}$  (green) interactions.



### **Comment on X-ray refinement special details for compound 7**

44 Uiso/Uij restrained atom sites, 48 distance or angle restraints and 428 least-squares restraints were used in the refinement.

The DFIX restraint was applied to the O-H Bonds with a distance of 0.87 Ang. for O-H bonds of compounds measured at the according temperature. (O5-H5, O8-H8 and O7-H7)

The SADI restraint was used for the chemically equivalent alcoholate ligands in the dimeric units and for the chemically similar alcohol ligands of the monomeric units.

The soft restraint DANG was used to fix problems with the tetrahedral angle of C3, C26 and C27 as well as avoiding the movement of the lightweight proton towards the Cu-atom.

The restraints SIMU (similar  $U_{ij}$  values for adjoining atoms) and DELU (rigid-bond) were applied to the  $U_{ij}$  values of all N, C and O atoms with the default esd. (SIMU \$N \$C \$O, DELU \$N \$O \$C). However, some atoms went to non-positive-definite and were further restrained with a soft restraint to be approximately isotropic with the ISOR restraint with default esd. (ISOR C9 O8 N6 N2 C29)

### **Comment on X-ray refinement special details for compound 8**

56 Uiso/Uij restrained atom sites, 67 distance or angle restraints and 811 least-squares restraints were used in the refinement.

The DFIX restraint was applied to the O-H Bonds with a distance of 0.87 Ang. for O-H bonds of compounds measured at the according temperature. (O5-H5, O6-H6, O7-H7 and O8-H8)

The SADI restraint was used for the disordered alcoholate ligands and the chemically equivalent but crystallographically independent alcoholate ligands in the dimeric units and for the chemically equivalent alcoholate ligands of the monomeric units.

The soft restraint DANG was used to fix problems with the tetrahedral angle of C3, C26 and C27 as well as avoiding the movement of the lightweight proton toward the Cu-atom

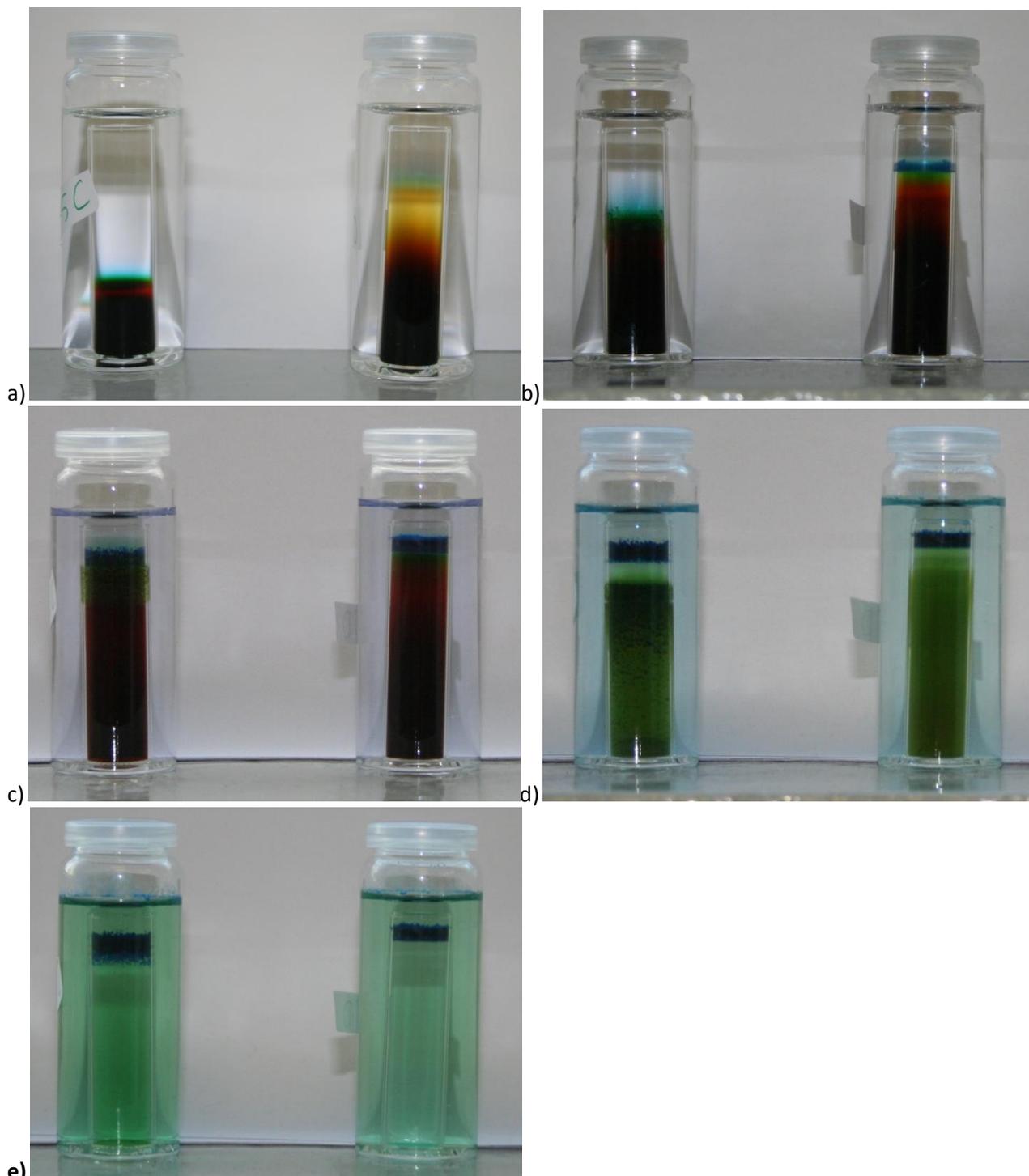
The restraints SIMU (similar  $U_{ij}$  values for adjoining atoms) and DELU (rigid-bond) were applied to the  $U_{ij}$  values of all N, C and O atoms with the default esd. (SIMU \$N \$C \$O, DELU \$N \$O \$C). However, some atoms went to non-positive-definite and were further restrained with a soft restraint to be approximately isotropic with the ISOR restraint with default esd. (ISOR C9A C20A C26A C16A O5A C8)

The EADP constraint was used for disordered atoms in the case that one part gave a sensible  $U_{ij}$  parameter and the other did not. (EADP O5 O5A, EADP C8A C8, EADP C18A C18, EADP C10A C10, EADP C12A C12, EADP C22A C22, EADP C4 C4A, EADP C11A C11)

### Photographs of reaction solutions:

General procedure for synthesis of single-crystalline materials of **1**, **3**, **7** and **8**:

A small glass vial with  $\text{CuBr}_2$  was placed into a bigger glass vial containing the amino alcohol. Both vials were carefully filled with methanol until the small vial was fully covered so that a connection for diffusion through the solvent was established (ca. 10 mL MeOH total).

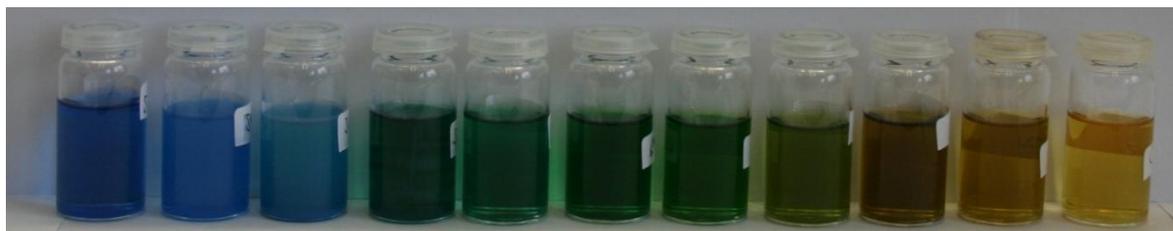


**Fig. S17** Development of reactant diffusion over time of abH with TEA present in the outer vial and  $\text{CuBr}_2$  in the inner vial. Difference between right and left experiment: in the right vial more disturbance occurred upon filling. Time: (a) after 2 hours, (b) after 1 day, (c) after 1 week, (d) after 1 month and 4 days, (e) after 4 months and 2 weeks. In (b) to (d), solid green intermediates have formed on the outside and inside of the vials and are clearly visible. Three months later (e), these have redissolved; only **3** is now present as a solid. No crystals suitable for X-ray single crystal diffractometry formed in this particular experiment.

**Solution colors for different Cu-to-amino alcohol ratios:**

- no triethylamin, TEA base added

- the amino alcohol can function as a ligand and – in excess – as a base for deprotonation



**Fig. S18** CuBr<sub>2</sub> to (*R*)-2-amino-1-butanol (*R*-abH) ratio from left to right

3:12 3:9 3:8 3:7 3:6 3:5 3:4 3:3 3:2 3:1.5 3:1

Cu : amino alcoholate : amino alcohol ratios in compounds

**1-6** (3:4:0)

**7** (6:4:3 = 3:3.5)

**8** (6:4:2 = 3:3)

necessary Cu-to-amino alcohol ratio when excess amino alcohol should also serve as a base for deprotonation:

Cu : amino alcoholate : amino alcohol (in compounds) : amino alcohol for deprotonation

**1-6** (3:4:0:4 = 3:8)

**7** (6:4:3:4 = 6:11 = 3:5.5)

**8** (6:4:2:4 = 6:10 = 3:5)

**Compound 9:**

**Table S3** Selected bond lengths and angles in compound **9**.<sup>a</sup>

bond lengths / Å		angles /°	
Cu-O1	1.926(11)	O1-Cu-O2	89.3(3)
Cu-O1	1.950(10)	O1-Cu-N1	86.3(4)
Cu-N1	1.966(9)	O2-Cu-N1	169.4(4)
Cu-N2	1.969(14)	N1-Cu-N2	100.1(3)
Cu-O3A	2.321(10)	O1-Cu-O3B	90.4(7)
Cu-O3B	2.315(19)	N1-Cu-O3B	99.5(7)
Cu-O12A	2.86(3)	O1-Cu-O3A	103.5(5)
		N1-Cu-O3A	87.3(4)
		O3A-Cu-O12A	162.02(4)
		O3B-Cu-O12A	173.57(8)

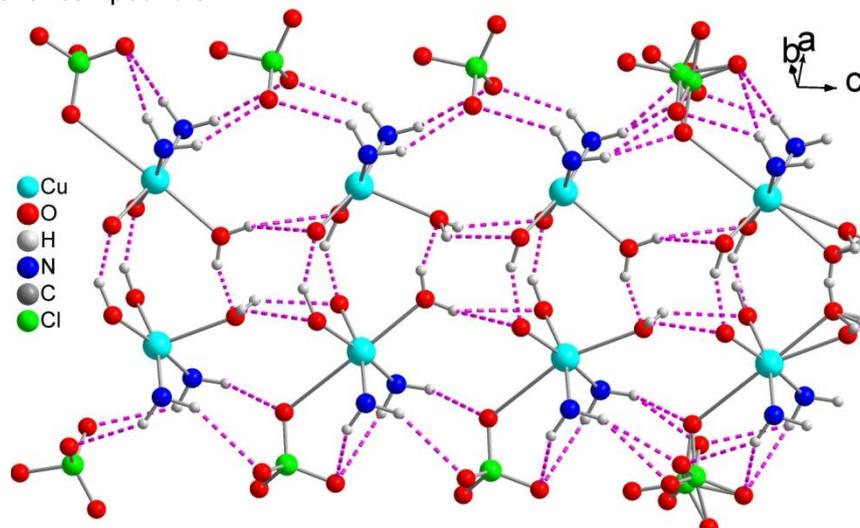
<sup>a</sup> The disordered water molecules have an occupancy of (O3A) 75% and (O3B) 25%, respectively. The orientation of O3B requires the water molecule of the second moiety to have the orientation of O3A as otherwise the O3B-O3B<sup>i</sup> contact would become too short (1.57(5) Å). However, O3A does not require the other orientation to be in O3B. The corresponding proton configuration for the constellation with an H-bond between O3A ... O3A<sup>i</sup> (2.8 Å) was not refined.

**Table S4** H-bonds in compound **9**.<sup>a</sup>

	O/N-H / Å	H...O / Å	O/N...O / Å	O/N-H...O /°	symm. transf.
O1-H11...O2 <sup>i</sup>	0.86(2)	1.66(14)	2.452(11)	151(27)	i = -x+1, -y+1, z
O2-H21...O1 <sup>i</sup>	0.95	1.64	2.452(11)	141.6	i = -x+1, -y+1, z
O3B-H33...O3A <sup>i</sup>	0.79(2)	1.49(2)	2.22(3)	152(6)	i = -x+1, -y+1, z
O3A-H*...O3A <sup>i</sup>			2.82(4)		i = -x+1, -y+1, z
N1-H1D...O12	0.92	2.47	3.13(2)	129.5	
N2-H2C...O11	0.92	2.23	3.03(3)	144.5	
N1-H1D...O14A	0.92	2.44	3.20(2)	140.4	
N2-H2C...O14A	0.92	2.42	3.19(2)	141.2	
O3A-H31...O1 <sup>ii</sup>	0.86(2)	2.28(7)	2.890(17)	128(8)	ii = x, y, z+1
O3A-H32...O2 <sup>ii</sup>	0.84(2)	2.32(7)	2.91(2)	128(8)	ii = x, y, z+1
O3B-H34...O1 <sup>ii</sup>	0.83(2)	2.55(4)	3.25(3)	143(2)	ii = x, y, z+1
O3B-H34...O1 <sup>ii</sup>	0.83(2)	2.55(4)	3.25(3)	143(2)	ii = x, y, z+1
N1-H1C...O12 <sup>ii</sup>	0.92	2.29	3.14(3)	152.0	ii = x, y, z+1
N2-H2D...O11 <sup>ii</sup>	0.92	2.43	3.34(3)	167.2	ii = x, y, z+1
N1-H1C...O12A <sup>ii</sup>	0.92	2.30	3.10(2)	146.1	ii = x, y, z+1
N2-H2D...O13A <sup>ii</sup>	0.92	2.53	3.37(3)	153.4	ii = x, y, z+1

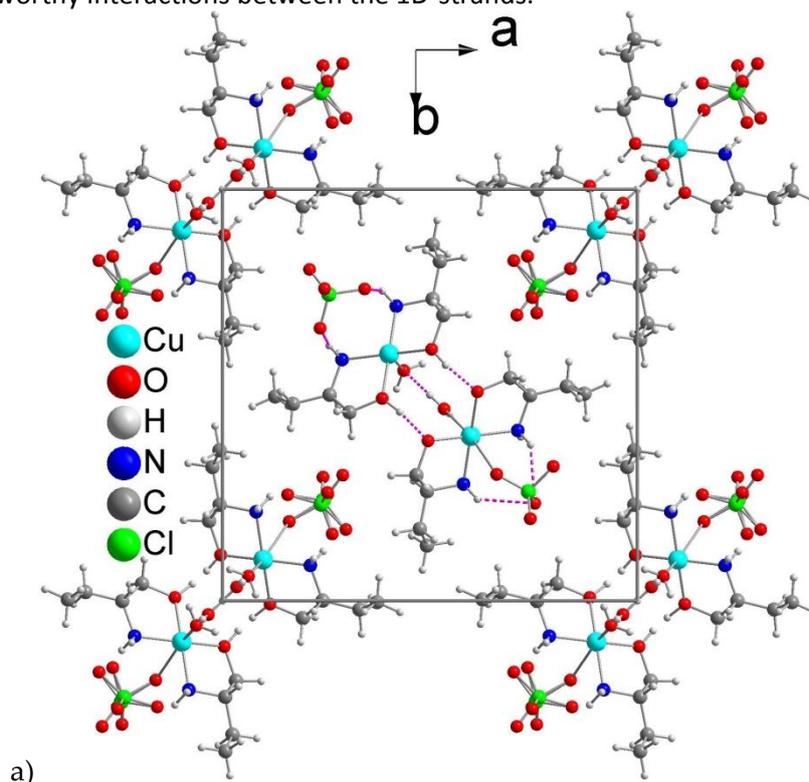
<sup>a</sup> For found and refined H-contacts the standard deviations are given; \* no H-atom for this H-bond refined.

Packing diagrams for compound **9**:



**Fig. S19** Hydrogen bonds (dashed pink lines) in compound **9** which connect the dimeric units into a supramolecular 1D strand. Dimeric units are shown with a random choice of either disordered orientation. The dimeric unit on the right is depicted with all disordered atoms. Carbon atoms are omitted for clarity. H-bond distances and angles are given in Table S4.

One dimeric unit of strand there from is surrounded by four dimeric units or strands there from (Fig. S20). There are no noteworthy interactions between the 1D-strands.



**Fig. S20** Section of the packing diagram in compound **9**. The dimeric unit in the center is shown with one type of disorder on each moiety; the other units are depicted with both possible disorders. H-Bonds are not shown in the disordered units for clarity.

## Comment on X-ray refinement special details for compound 9

22 Uiso/Uij restrained atom sites, 31 distance or angle restraints and 297 least-squares restraints were used in the refinement

The SADI restraint was used for the disordered perchlorate anion to fix the tetrahedral geometry and adapt the two disordered molecules to be the same geometry.

The displacement parameters of the two disordered molecules were constrained with the EADP constraint to have the same displacement parameters.

The geometry of the two chemically equivalent alcohol/alcoholate ligands was restrained to be the same with the SADI restraint. The O-H bond of the alcohol ligand was restrained with the DFIX 0.84 to the distance suggested for the measuring temperature. Furthermore, the shift of the protons towards the heavy Cu atom was prevented with DANG restraints.

The two disordered water molecules were adapted to have the same H-O-H angles with DANG restraints. The O-H bond length was restrained with DFIX 0.84. The tilting of the water molecule to the heavy Cu atom was prevented and the mirror symmetry for the coordinated water molecule to a chemical reasonable position was achieved with SADI restraints. The Uij of the water molecules were adapted to be the same with the EADP constraint.

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