

SUPPORTING INFORMATION

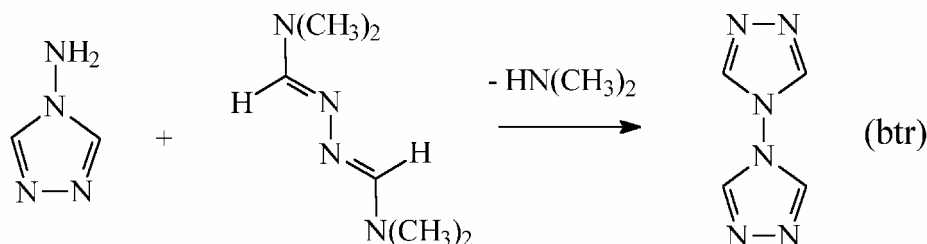
Metal-Organic Frameworks Incorporating $\text{Cu}_3(\mu_3\text{-OH})$ Clusters

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1. Synthesis

4,4'-Bi(1,2,4-triazole) (*btr*)



The ligand was prepared according to the above scheme using the literature method (R. K. Bartlett, I. R. Humphrey, *J. Chem. Soc., Section C*, **1967**, (17), 1664).

A stirred mixture of 4-amino-4*H*-1,2,4-triazole (8.41 g, 0.100 mol), dimethylformamidine (14.2 g, 0.100 mol) and TsOH (0.800 g, 4.64 mmol) was refluxed in toluene (40 mL) for 65 h (oil bath temperature 130°C). The resulted precipitate was filtered off, washed with toluene (10 mL), ethanol (2 x 5 mL) and ether (5 mL) that afforded the desired product (7.94 g, 58%).

Coordination compounds:

Synthesis of $[\{\text{Cu}_3(\mu_3\text{-OH})\}\{\text{Cu}_3(\mu_3\text{-O})\}(\mu_4\text{-btr})_3(\text{H}_2\text{O})_4(\text{OH})_2\text{Cl}_6]\text{Cl}\cdot 0.5\text{H}_2\text{O}$ **1**: The compound was prepared using a layering technique. The reactant solutions were layered in the following order: *btr* (27.2 mg, 0.20 mmol) in water (1 mL), then two middle layers of aqueous methanol (2.5 mL of 1:1 v/v $\text{CH}_3\text{OH}/\text{H}_2\text{O}$, and 2.5 mL of with a ratio of 2:1 v/v $\text{CH}_3\text{OH}/\text{H}_2\text{O}$),

and top-layered with a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (34.0 mg, 0.20 mmol) in 3 mL methanol. Slow interdiffusion of the reaction components at rt for a period of 9-10 d afforded large compact green octahera of the complex **1** (60%) in a mixture with a very minor co-product $\text{Cu}_3\text{Cl}_6(\text{btr})_4$ (blue plates, *ca.* 10%).

Anal. (Carlo Erba Str.): For **1**, $\text{C}_{12}\text{H}_{24}\text{Cl}_7\text{Cu}_6\text{N}_{18}\text{O}_{8.5}$, Calcd., %: C, 12.15; H, 2.04; N, 21.27. Found, %: C, 12.04; H, 1.92; N, 21.06. For $\text{Cu}_3\text{Cl}_6(\text{btr})_4$, $\text{C}_{16}\text{H}_{16}\text{Cl}_6\text{Cu}_3\text{N}_{24}$, Calcd., %: C, 20.27; H, 1.70; N, 35.47. Found, %: C, 20.48; H, 1.84; N, 35.60.

The same complex **1** crystallizes from aqueous solution of the components under slow evaporation at rt for several weeks, in a mixture with blue unidentified material. However, when crystallization occurs relatively fast, it was possible to isolate complex **3** in high yield.

Synthesis of $[\{\text{Cu}_3(\mu_3\text{-OH})\}_2(\mu_3\text{-btr})_6(\mu_4\text{-btr})(\mu\text{-Cl})\text{Cl}_4]\text{Cl}_5 \cdot 8\text{H}_2\text{O}$ **3**:

Solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (17.0 mg, 0.10 mmol) and btr (13.6 mg, 0.10 mmol) in 1 mL water, in a 5 mL vial, was placed in a tightly stoppered 250 mL TLC chamber containing 30 mL of 1:1 v/v ether-THF mixture. A diffusion of ether-THF vapor, at 25-27°C, into the aqueous solution of the reactants affords crystallization of complex **3**, for a period of 10-12 h. The yield was 90% (green plates).

Anal. (Carlo Erba Str.): For **3**, $\text{C}_{28}\text{H}_{46}\text{Cl}_{10}\text{Cu}_6\text{N}_{42}\text{O}_{10}$, Calcd., %: C, 18.01; H, 2.48; N, 31.52. Found, %: C, 17.86; H, 2.34; N, 31.12.

Synthesis of $[\{\text{Cu}_3(\mu_3\text{-OH})\}_2(\mu_3\text{-btr})_6(\mu_4\text{-btr})(\mu\text{-Br})\text{Br}_4]\text{Br}_5 \cdot 6\text{H}_2\text{O}$ **2**:

The compound was prepared using a layering technique.

The reactant solutions were taken in the following order: btr (13.6 mg, 0.10 mmol) in water (0.5 mL) and two middle layers of aqueous ethanol - 2.5 mL of 4:1 v/v EtOH/H₂O and 2.5 mL of 8:1 v/v EtOH/H₂O were top-layered with a solution of CuBr_2 (22.3 mg, 0.10 mmol) in 3 mL ethanol. Slow interdiffusion at rt for a period of 8-10 d afforded two crystalline phases: green well developed plates of complex **3** as a major product (yield 40%) and unidentified blue polycrystalline material - minor product.

Anal. (Carlo Erba Str.): For **2**, $\text{C}_{28}\text{H}_{42}\text{Br}_{10}\text{Cu}_6\text{N}_{42}\text{O}_8$, Calcd., %: C, 14.78; H, 1.86; N, 25.86. Found, %: C, 14.49; H, 1.91; N, 25.74.

2. Crystallography

The intensity data were collected at 213 K on a Stoe Imaging Plate Diffraction System [1] using $\text{MoK}\alpha$ graphite monochromated radiation ($\lambda = 0.71073$ Å): ϕ oscillation scans 0–180°, step $\Delta\phi = 1.0^\circ$ for compounds **1**, **3** and $\Delta\phi = 0.8^\circ$ for compound **2**. The structures were solved by

direct methods and refined in the anisotropic approximation using SHELXS-86 [2] and SHELXL-97 [3]. Details are given below.

Graphical representation of the crystal structures was made using program Diamond [4].

1. Stoe & Cie (2000). *IPDS Software*. Stoe & Cie GmbH, Darmstadt, Germany.
2. G.M. Sheldrick, *Acta Crystallogr.*, 1990, **A46**, 467.
3. G.M. Sheldrick, SHELXL97, A system of computer programs for X-ray structure determination, University of Göttingen, Göttingen, Germany, 1997.
4. K. Brandenburg, Diamond 2.1c, Crystal Impact GbR, Bonn, 1999.

Refinement of the structures

Structure [$\{\text{Cu}_3(\mu_3\text{-OH})\}\{\text{Cu}_3(\mu_3\text{-O})\}(\mu_4\text{-btr})_3(\text{H}_2\text{O})_4(\text{OH})_2\text{Cl}_6\}\text{Cl}\cdot 0.5\text{H}_2\text{O}$ 1

All non-hydrogen atoms were refined anisotropically, all CH hydrogens were placed in calculated positions with isotropic U values at 1.2 times of equivalent isotropic U value of the corresponding carbon atom. Non-coordinated chloride anion and water molecule were disordered forming contact Cl---O 1.98 Å, and they were refined with partial occupancies 0.5. For the refinement of the structure and assignment of the composition the following aspects were important:

First, two tricopper clusters afford tight parallel stack. Whithin the stack, two μ_3 -oxygen atoms deviate from corresponding Cu_3 planes by 0.49 Å towards each other and appear in a closest possible contact at O---O 2.712 Å (See Figure 1, main text). This clearly indicates hydrogen bonding O-H---O that occurs between μ_3 -hydroxo and μ_3 -oxo moieties. The latter are related by symmetry and therefore they are not distinguishable structurally. It is worth noting also that $\mu_3\text{-O-Cu}$ bond lengths in present case ($3\times 2.026(2)$ Å) are shorter than those for complex 2: ($2\times 2.040(3)$, 2.033(5) Å).

Second, from charge compensation considerations, part of axially coordinated ligands (one of three equivalents per tricopper cluster) are hydroxo groups and the remaining ones are water molecules. These three positions of the oxygen atoms are related by three-fold axis and they are structurally equivalent. We did not register any other reasonable peaks of the electron density outside the framework in the course of the structure refinement. System of eight

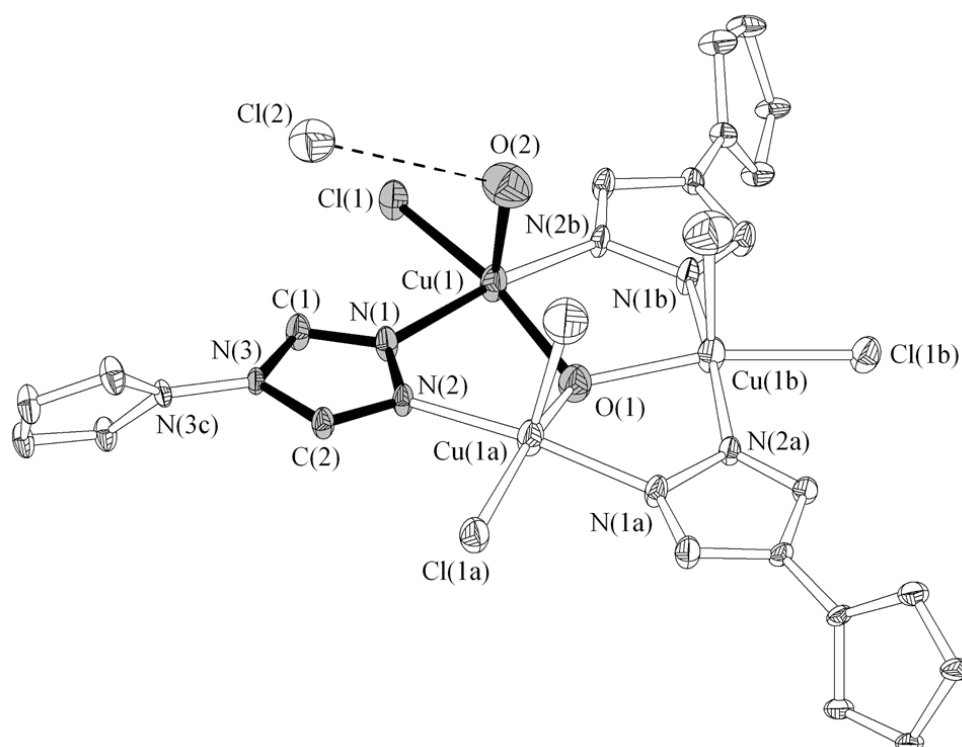


Figure S1. Atom labeling scheme for structure

$[\{\text{Cu}_3(\mu_3\text{-OH})\}\{\text{Cu}_3(\mu_3\text{-O})\}(\mu_4\text{-btr})_3(\text{H}_2\text{O})_4(\text{OH})_2\text{Cl}_6]\text{Cl}\cdot 0.5\text{H}_2\text{O}$ **1**. Thermal ellipsoids are at 50% probability level and hydrogen atoms are omitted. Unique part of the structure is shaded grey and with bold lines. Symmetry codes used to generate equivalent atoms:

a) $-0.5+z, 0.5+x, y$; b) $-0.5+y, z, 0.5+x$; c) $-0.75+y, 0.75+x, 1-z$.

interpenetrating frameworks occupies 92.4% of the space (Platon) and the remaining volume is populated with non-coordinated chloride ions and water of crystallization (99.2% of the space in total).

Third, four trinuclear clusters are arranged in such a manner that they appear to be situated on faces of tetrahedron with edge of ca. 18 Å. This is very characteristic pattern for packing of large nearly planar moieties possessing trigonal symmetry. See for example comparable 18-crown-6 systems (F. Rieger, A.-V. Mudring, *Inorg. Chem.* **2005**, 44, 9340; K.V. Domasevitch, J.A. Rusanova, J. Sieler, V.N. Kokozay, *Inorg. Chim. Acta*, **1999**, 293, 234).

In present case, such the pattern is facilitated by OH---O hydrogen bonding that occurs between axially coordinated ligands. Twelve oxygen atoms (from four tricopper clusters) are arranged into distorted icosahedron (See Fig. 3 of main text) and appear in close contact. Each oxygen atom at the vertex of the icosahedron has one neighbor at 2.74 Å, two neighbors at 3.02 Å (within single tricopper cluster) and two distal O---O contacts at 3.65 Å. Non-coordinated chloride ions (two equivalents per oxygen icosahedron) form triple contact Cl---O (3.15 Å)

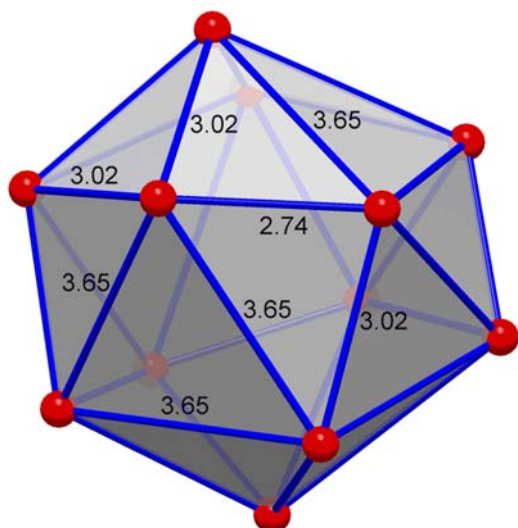


Figure S2. View of icosahedron sustained with coordinated oxygen atoms of four tricopper clusters in the structure **1**. Note that part of O---O separations (edges of the icosahedron) are reasonable for hydrogen bonding.

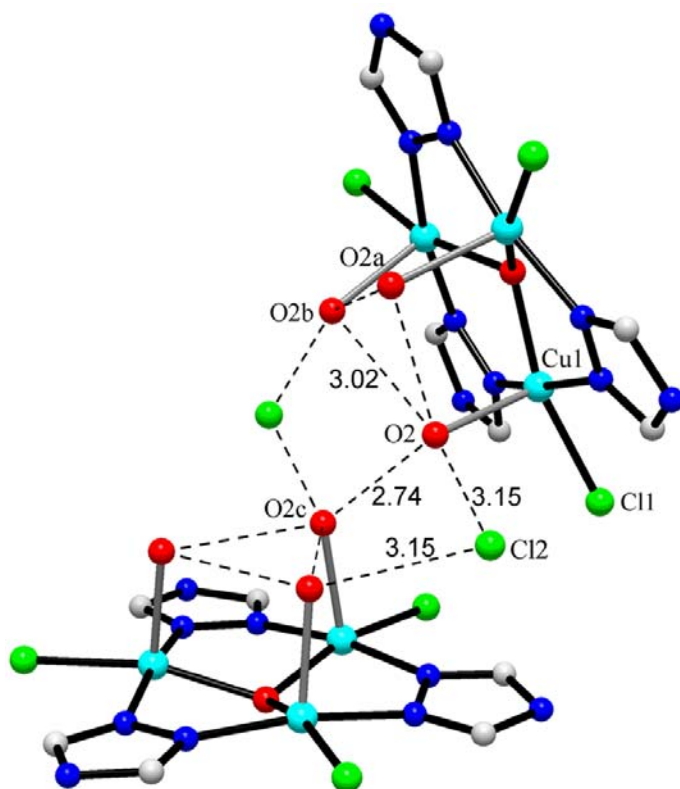


Figure S3. Possible hydrogen bonding that occurs between neighboring tricopper clusters and non-coordinated chloride ions.

centering a larger face of the icosahedron. Such separations are typical for hydrogen bonding OH---Cl in hydrated metal chlorides.

Clear attribution of the hydrogen bonding scheme within the icosahedron is complicated due to a high symmetry of the array and total structural equivalence of eight water and four hydroxo ligands sustaining icosahedron. Shorter edges of the octahedron (O---O 2.74 Å) suggest characteristic hydrogen bonding. Weaker hydrogen bonding is likely occurs also between axial oxygen atoms of the discrete tricopper clusters (O---O 3.02 Å). Additional factor for such suggestion is a certain attraction of these axial ligands. This is reflected by shortening of O2---O2' separations (3.02 Å) with respect to corresponding Cu1---Cu1' distances within the trimer (3.41 Å). Also, Cl1-Cu1-O2 angles (98.5°) appreciably exceed 90°. Thus the Cu1-O2 vectors are not orthogonal to the Cu₃ plane and they adopt orientation facilitating closer situation of three symmetry equivalent O2 atoms.

Structure [$\{\text{Cu}_3(\mu_3\text{-OH})\}_2(\mu_3\text{-btr})_6(\mu_4\text{-btr})(\mu\text{-Br})\text{Br}_4\}\text{Br}_5\cdot 6\text{H}_2\text{O}$ 2

All non-hydrogen atoms were refined anisotropically, all CH hydrogens were placed in calculated positions with isotropic U values at 1.2 times of equivalent isotropic U value of the corresponding carbon atom.

There were certain problems with disorder of heavy bromine atoms, a set of solvate water molecules and one coordinated bitriazole ligand. Part of the bromide ions were coordinated to copper atoms, however, they are situated in axial positions and are only weakly bound (Cu-Br 2.67 and 2.78 Å). One bromide ligand is bridging between copper atoms of two tricopper clusters and is ordered, while Br(1) atom is disordered between two positions (one – coordinated, second – much distal, Cu-Br1A 4.16 Å). Refined partial occupancies factors were 0.88 and 0.12. Additional non-coordinated bromide ion Br(3) resides in general position (this corresponds to two equivalents per tricopper cluster), this ion is ordered, it forms set of weak hydrogen bonds CH---Br with the triazole groups (C---Br 3.52, 3.62 Å) and possesses normal parameters for thermal motion. Remaining non-coordinated bromide ion (0.5 equivalent per tricopper cluster) was disordered by several positions and these were overlapped with the peaks corresponding to water of crystallization. It was not possible to resolve this scheme. Therefore, the remaining disordered electron density was successfully modeled using *Squeeze* (A. L. Spek, PLATON/PLUTON, Jan. 1999, *Acta Crystallogr. Sect. A.* 1990, **46**, C-34) that decreased convergence factor to R1 from 0.092 to 0.049.

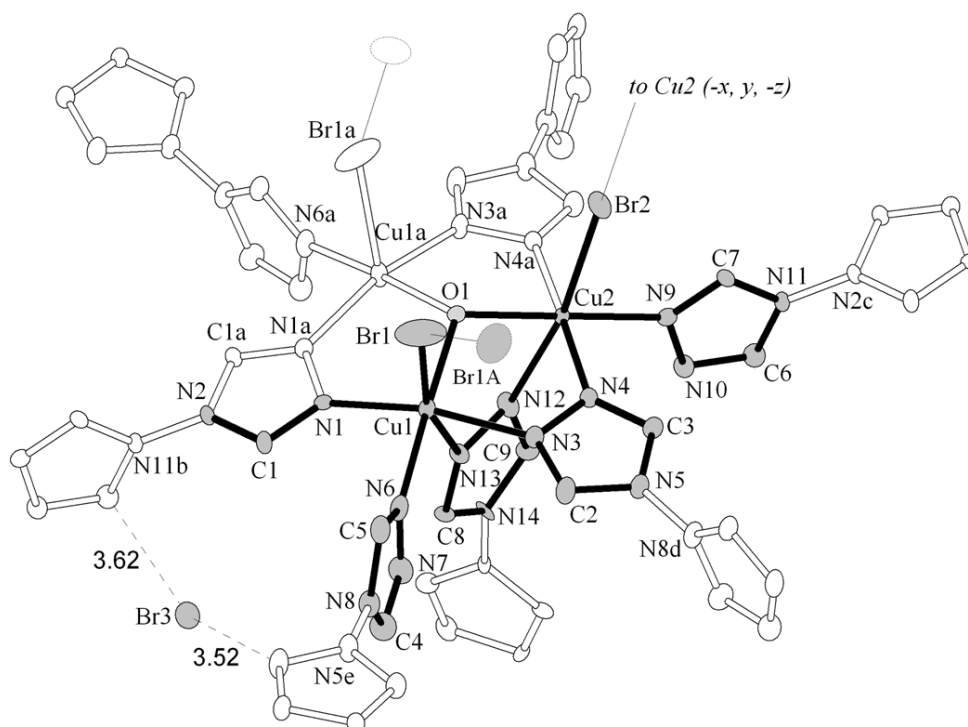


Figure S4. Atom labeling scheme for structure $[\{\text{Cu}_3(\mu_3\text{-OH})\}_2(\mu_3\text{-btr})_6(\mu_4\text{-btr})(\mu\text{-Br})\text{Br}_4]\text{Br}_5 \cdot 6\text{H}_2\text{O} \mathbf{3}$ (hydrogen atoms are omitted). Thermal ellipsoids are at 35% probability level and unique part of the structure is shaded grey and with bold lines. Symmetry codes used to generate equivalent atoms: a) $x, -y, z$; b) $-1+x, y, z$; c) $1+x, y, z$; d) $0.5+x, 0.5-y, z$; e) $-0.5+x, 0.5-y, z$.

The bitriazole ligand that is coordinated to the tricopper cluster at the axial site was also disordered. Scheme of this disorder is very clear and it is presented in Figure S5. The disorder originates in availability of three equivalent copper atoms as coordination acceptors for each pair of triazole donors, and thus atom N12 is coordinated to Cu2 and is ordered, while atom N13 is disordered over two positions related by a mirror plane (and completes coordination environment of Cu1 or Cu1a atoms). Thus two components of the disorder are related by a mirror plane and they have equal contributions 0.5.

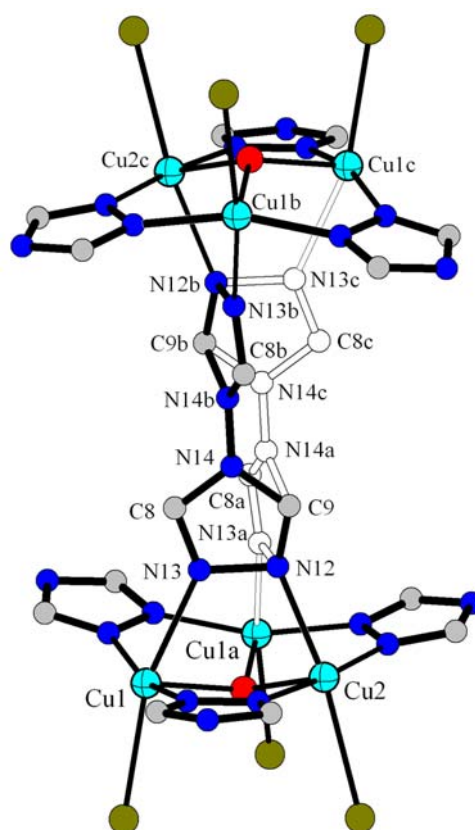


Figure S5. Refined disordering scheme for μ_4 -btr ligand in structure $[\{Cu_3(\mu_3-OH)\}_2(\mu_3-btr)_6(\mu_4-btr)(\mu-Br)Br_4]Br_5 \cdot 6H_2O$ **2**. Symmetry codes used to generate equivalent atoms: a) $x, -y, z$; b) $-x, y, 1-z$; c) $-x, -y, 1-z$. Atoms C9 and N12 have occupancy factors 1.0 and contribute to both components of the disorder, while atoms N13, C8 and N14 have partial occupancy factors 0.5.

Structure $[\{Cu_3(\mu_3-OH)\}_2(\mu_3-btr)_6(\mu_4-btr)(\mu-Cl)Cl_4]Cl_5 \cdot 8H_2O$ **3**

The refinement was standard: all non-hydrogen atoms (with exception of solvate water molecules) were refined anisotropically, all CH hydrogens were placed in calculated positions with isotropic U values at 1.2 times of equivalent isotropic U value of the corresponding carbon atom. μ_3 -OH hydrogen atoms were added geometrically with isotropic U values at 1.5 times of the corresponding oxygen atom.

Only one of eight unique solvate water molecules was refined isotropically. The hydrogen atoms of the solvate water were not located and were not added. There are five unique non-coordinated chloride ions, three of which were disordered over closely situated positions and only major component of the disorder was refined isotropically.

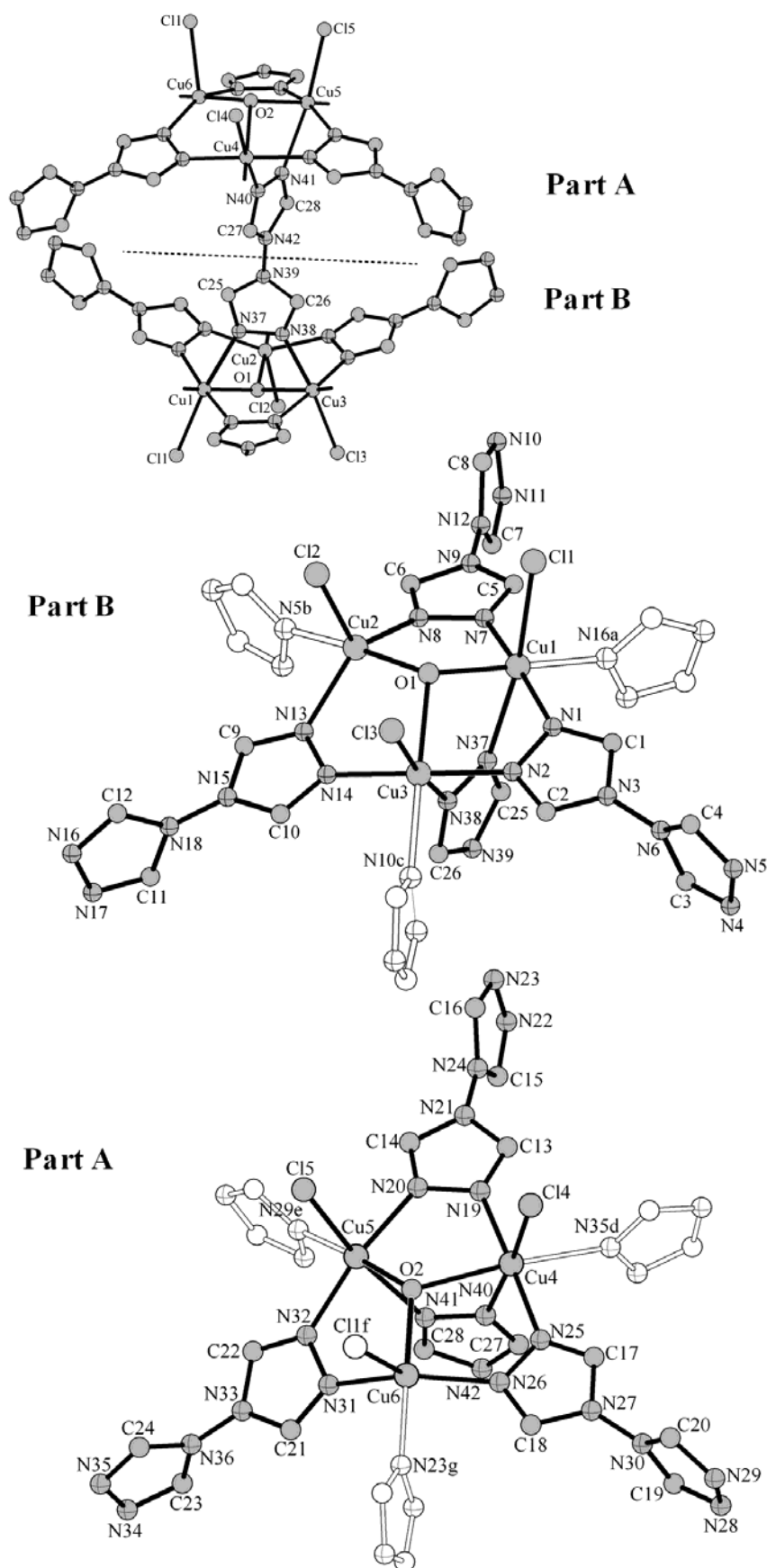


Figure S6. Atom labeling scheme for structure $[\{Cu_3(\mu_3-OH)\}_2(\mu_3-btr)_6(\mu_4-btr)(\mu-Cl)Cl_4]Cl_5 \cdot 8H_2O \cdot 2$ (hydrogen atoms are omitted). Unique part of the structure is shaded grey and with bold lines. Symmetry codes used to generate equivalent atoms: a: $x, -1+y, z$; b: $0.5+x, 0.5+y, z$; c: $-0.5+x, 0.5+y, z$; d: $-0.5+x, -0.5+y, z$; e: $x, 1+y, z$; f: $x, -1-y, -0.5+z$; g: $0.5+x, -0.5+y, z$.

This structure may be related with the bromide analog 2. In this case the additional bitriazole ligand connecting pair of the tricopper clusters is ordered (unlike disorder in structure 2) and this led to elimination of the inversion symmetry of the structure and to doubling of the asymmetric unit.