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Metal–organic frameworks incorporating $Cu_3(\mu_3\text{-}OH)$ clusters†‡

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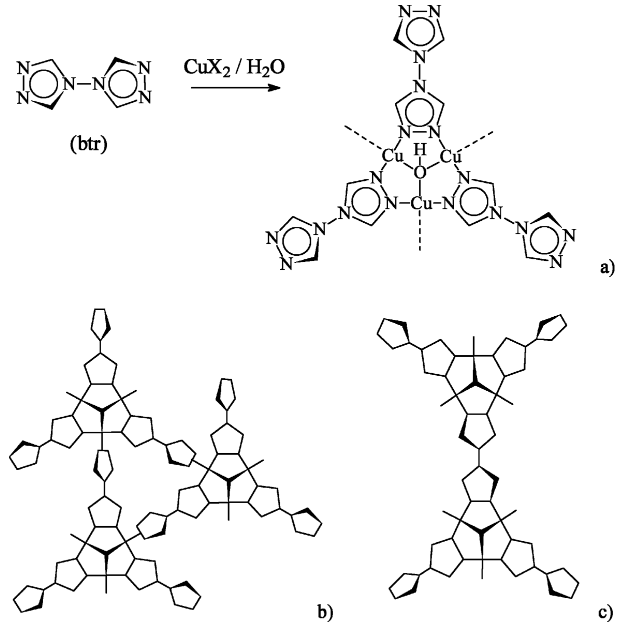
Interaction of 4,4′-bi(1,2,4-triazole) (btr) with copper(II) chloride (bromide) in aqueous or aqueous alcohol media led to a series of coordination polymers featuring the formation of μ_3-hydroxotricopper(II) clusters and their integration into 3D frameworks. These unprecedented structures originate in the propagation of trigonal hydroxotricopper(II) clusters bridged by tri- or tetradentate organic ligands. Complex $[\{Cu_3(\mu_3\text{-}OH)\}\{Cu_3(\mu_3\text{-}O)\}(\mu_4\text{-}btr)_3(H_2O)_4(OH)_2Cl_6]Cl\cdot0.5H_2O$ adopts a structure of $SrSi_2$ topology, with eight-fold interpenetration of the coordination frameworks. The structure of $[\{Cu_3(\mu_3\text{-}OH)\}_2(\mu_3\text{-}btr)_6(\mu_4\text{-}btr)(\mu\text{-}X)X_4]X_5\cdot nH_2O$ ($X = Br, n = 6; X = Cl, n = 8$) involves 2D coordination layers $[\{Cu_3(\mu_3\text{-}OH)\}(\mu_3\text{-}btr)_3]_n$ with an exceptional (3,6)-net topology, which are cross-linked by tetradentate btr ligands and bridging chloride (bromide) ions.

Introduction

In recent years, metal–organic frameworks[1] containing coordinatively unsaturated metal centers have received significant attention[2] due to the possibility of evaluating a fundamental host–guest interaction, to perform chemical sensing, hydrogen storage[3] and catalysis.[4] Increases in efficiency and selectivity of such 3D host lattices may arise *via* the use of receptor centers, in which the coordination core provides multiple binding sites, as may be compared with simpler axially unsaturated copper(II) diketonates, porphyrins and related systems.[5] However, in most polynuclear species the metal centers are blocked by ligation (as occurs for μ_4-oxo zinc carboxylates) and therefore are almost excluded from direct interaction with potential substrates.[6] Unlike these species, nearly planar μ_3-hydroxo trimetallic clusters retain steric accessibility of the multiple metal centers at two axial sides, they display potential in catalysis and in biology (*e.g.*, reactions provided by copper blue oxidases)[7] and they could be best applied to the functionalization of metal–organic polymers. Herein, we report the utilisation of this coordination archetype as an unprecedented secondary building block[5,8] for the pre-programmed synthesis of framework solids.

Results and discussion

An efficient design strategy was based upon the construction of the μ_3-hydroxotrimetallic core using suitable η^2-heterocyclic bridges that also provide further integration of the cluster in a framework. A series of molecular tricopper(II) clusters with 1,2,4-triazoles[9] and pyrazolide ions[10] supply a paradigmatic precedent for such a combination of inorganic and organic bridges, while a doubled functionality, as provided by the 4,4′-bi(1,2,4-triazole) ligand (btr), allows the generation of the polymer by propagation of the trigonal geometry of the molecular unit (Scheme 1). In this case the twisted conformation of the bitriazole[11] facilitates control over the entire connectivity: it predetermines an orthogonal orientation for the successively bridged tricopper clusters and generation of a 3D three-connected net.



Scheme 1 The μ_3-hydroxo cluster formed by btr ligands and copper(II) chloride or bromide (a) and target polymeric motifs that imply self-association (b) or further aggregation (c) of the tricopper clusters.

The framework structure of $[\{Cu_3(\mu_3\text{-}OH)\}\{Cu_3(\mu_3\text{-}O)\}(\mu_4\text{-}btr)_3(H_2O)_4(OH)_2Cl_6]Cl\cdot0.5H_2O$ (**1**) originates in a combination of these design prerequisites, it exists in the form of a regular 3D net of (10,3)-a topology (usually related to the $SrSi_2$ structure; 10^3 tile) that implies the tricopper clusters are three-connected nodes (Fig. 1, 2). This array may be best compared with a hydrogen bonded framework formed by 4,4′-bipyrazole, in which the pyrazole functions adopt a characteristic trimeric pattern.[12]

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† The HTML version of this article has been enhanced with additional colour.

‡ Electronic supplementary information (ESI) available: Crystal structure determination and refinement details for **1–3**. See DOI: 10.1039/b604804h

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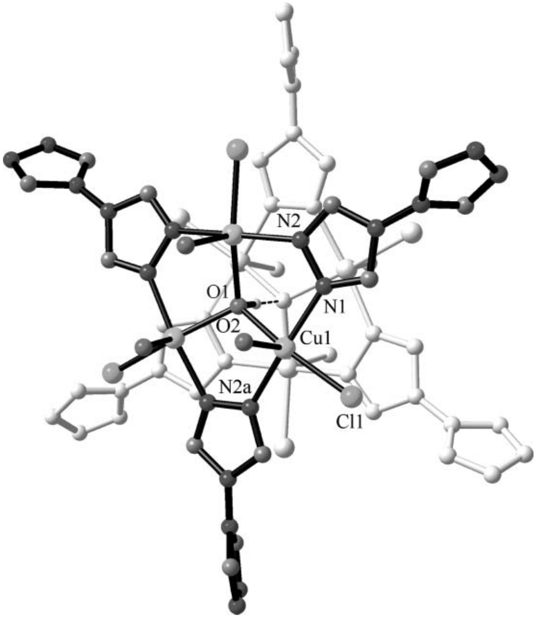

Fig. 1 Association of μ_3-hydroxo and μ_3-oxo clusters sustaining structure **1** by OH···O hydrogen bonding.

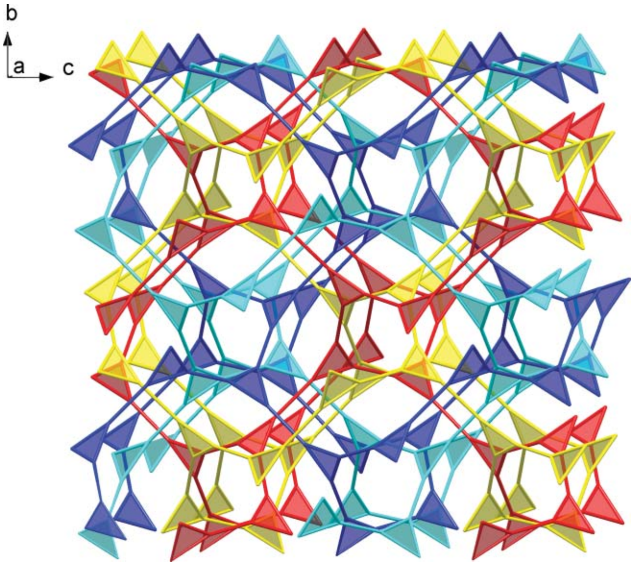

Fig. 2 Fragment of structure **1** showing four (out of eight) interpenetrating (10,3)-a nets. The triangles represent the tricopper clusters linked by bitriazole connectors.

Table 1 Selected bond distances (Å) and angles (°) for complexes **1–3**

$[\{Cu_3(\mu_3\text{-}OH)\}\{Cu_3(\mu_3\text{-}O)\}(\mu_4\text{-}btr)_3(H_2O)_4(OH)_2Cl_6]Cl\cdot0.5H_2O^a$ (**1**)			
Cu(1)–N(1)	2.004(4)	O(1)–Cu(1)–Cl(1)	163.7(2)
Cu(1)–N(2a)	1.996(4)	N(1)–Cu(1)–Cl(1)	89.7(1)
Cu(1)–O(1)	2.026(2)	N(1)–Cu(1)–N(2a)	170.2(2)
Cu(1)–O(2)	2.200(5)	N(1)–Cu(1)–O(1)	88.2(1)
Cu(1)–Cl(1)	2.294(1)	N(1)–Cu(1)–O(2)	90.7(2)
Cu(1)–O(1)–Cu(1a)	114.4(2)	O(1)–Cu(1)–O(2)	97.7(3)
$[\{Cu_3(\mu_3\text{-}OH)\}_2(\mu_3\text{-}btr)_6(\mu_4\text{-}btr)(\mu\text{-}Br)Br_4]Br_5\cdot6H_2O$ (**2**)			
Cu(1)–O(1)	2.040(3)	Cu(2)–N(12)	2.284(7)
Cu(1)–N(1)	2.000(5)	Cu(2)–Br(2)	2.779(1)
Cu(1)–N(3)	2.012(5)	Cu(1)–O(1)–Cu(2)	113.9(1)
Cu(1)–N(6)	2.021(5)	N(1)–Cu(1)–O(1)	91.1(2)
Cu(1)–N(13)	2.440(9)	N(1)–Cu(1)–N(3)	161.4(2)
Cu(1)–Br(1)	2.672(1)	O(1)–Cu(1)–Br(1)	90.2(1)
Cu(2)–O(1)	2.033(5)	N(4)–Cu(2)–O(1)	90.3(1)
Cu(2)–N(4)	2.012(4)	N(9)–Cu(2)–O(1)	179.5(2)
Cu(2)–N(9)	2.025(7)	O(1)–Cu(2)–Br(2)	88.9(1)
$[\{Cu_3(\mu_3\text{-}OH)\}_2(\mu_3\text{-}btr)_6(\mu_4\text{-}btr)(\mu\text{-}Cl)Cl_4]Cl_5\cdot8H_2O$ (**3**)^b			
Cu(1)–Cl(1)	2.601(3)	Cu(4)–N(25)	2.037(10)
Cu(1)–O(1)	1.986(7)	Cu(4)–N(35d)	2.335(11)
Cu(1)–N(1)	2.047(10)	Cu(4)–N(40)	2.055(10)
Cu(1)–N(7)	2.014(10)	Cu(5)–Cl(5)	2.539(4)
Cu(1)–N(16a)	1.990(9)	Cu(5)–O(2)	1.963(8)
Cu(1)–N(37)	2.339(10)	Cu(5)–N(20)	2.108(10)
Cu(2)–Cl(2)	2.359(4)	Cu(5)–N(29e)	2.012(10)
Cu(2)–O(1)	1.973(9)	Cu(5)–N(32)	2.038(11)
Cu(2)–N(5b)	1.998(11)	Cu(5)–N(41)	2.416(10)
Cu(2)–N(8)	2.044(10)	Cu(6)–Cl(1f)	2.427(3)
Cu(2)–N(13)	2.135(9)	Cu(6)–O(2)	1.977(8)
Cu(3)–Cl(3)	2.288(3)	Cu(6)–N(26)	2.056(10)
Cu(3)–O(1)	2.296(10)	Cu(6)–N(23g)	2.025(11)
Cu(3)–N(2)	2.015(9)	Cu(6)–N(31)	2.039(10)
Cu(3)–N(10c)	2.283(13)	Cu(1)–O(1)–Cu(2)	121.1(4)
Cu(3)–N(14)	1.997(10)	Cu(1)–O(1)–Cu(3)	106.5(4)
Cu(3)–N(38)	2.109(9)	Cu(2)–O(1)–Cu(3)	114.1(4)
Cu(4)–Cl(4)	2.279(3)	Cu(4)–O(2)–Cu(5)	106.7(3)
Cu(4)–O(2)	2.334(8)	Cu(4)–O(2)–Cu(6)	111.6(3)
Cu(4)–N(19)	2.012(10)	Cu(5)–O(2)–Cu(6)	121.2(5)

[a] a: −0.5 + *y*, *z*, 0.5 + *x*. [b] 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*.

Though the framework solely occupies only 11.6% of the space,[13] the entire structure was generated by interpenetration of eight identical frameworks (four pairs of opposite chirality); this is the highest degree of interpenetration of (10,3)-a nets observed in a crystal structure[14] and the second known example of class IIIb interpenetration[15] where four pairs of enantiochiral nets are present.

A salient feature of the structure, unprecedented for molecular systems, consists of the association between the tricopper clusters. The short separation between pairs of μ_3-oxygen atoms, which are shifted by 0.49 Å from the Cu_3 planes towards each other (O···O 2.712 Å), indicates that directional hydrogen bonding occurs between the μ_3-hydroxo- and μ_3-oxo-moieties (*i.e.* $Cu_3OH–OCu_3$) and facilitates very dense packing. When this bond is considered for overall connectivity, the interpenetration disappears and a peculiar and unique uninodal uniform self-catenated net is found with topology Schläfli symbol $\{8^6\}$.

The copper ions adopt a distorted square pyramidal coordination, with equatorial μ_3-oxygen, two nitrogen atoms and chloride ligand, and distal apical water (hydroxo) ligands (Table 1). The trinuclear clusters adopt the packing pattern, which is very characteristic of large nearly planar moieties possessing trigonal symmetry, for example some of the 18-crown-6 complexes.[16] In this way four clusters are situated on the faces of a tetrahedron with edges of *ca.* 18 Å and twelve apical oxygen atoms reside inside the cage and appear to be arranged in a distorted icosahedron (Fig. 3). The shorter edges of this unprecedented ensemble (O···O 2.74, 3.02 and 3.65 Å) are reasonable for hydrogen bonding.

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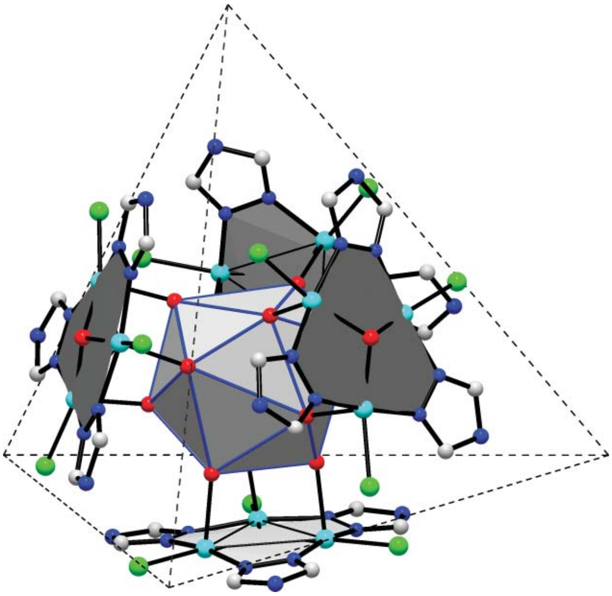

Fig. 3 Fragment of the structure **1**, which shows mode of packing of four symmetry related tricopper clusters.

The rich coordination functionality of the tricopper synthon, which involves three chlorides in the equatorial plane and distal apical aqua (hydroxo) ligands, provides wider possibilities for framework design as was demonstrated by the structure of $[\{Cu_3(\mu_3\text{-}OH)\}_2(\mu_3\text{-}btr)_6(\mu_4\text{-}btr)(\mu\text{-}Br)Br_4]Br_5\cdot 6H_2O$ (**2**). Thus the chloride ligands in **1**, which are *trans* with respect to the μ_3-oxygen atoms, are only weakly bound (2.294(1) Å) due to a possible interference with the adjacent triazolyl groups and therefore this position is hardly suited for a larger bromide ion. Under elimination of the terminal ligands from these positions, as may be anticipated for the copper(II) bromide system, the molecular units $[Cu_3(\mu_3\text{-}OH)(btr)_3]^{5+}$ become self-complementary since they combine either acceptor or donor sites (unsaturated equatorial coordination positions and the outer triazole-N donors) (Scheme 1,b). Thus generation of the $\{[Cu_3(\mu_3\text{-}OH)(btr)_3]\}_n$ planar (3,6)-network by simple self-association (Fig. 4) involves the ligands as tridentate donors, with only one η^2-triazole function engaged within the tricopper cluster. It is worth noting that such a structure may be reproduced also with copper chloride, $[\{Cu_3(\mu_3\text{-}OH)\}_2(\mu_3\text{-}btr)_6(\mu_4\text{-}btr)(\mu\text{-}Cl)Cl_4]Cl_5\cdot 8H_2O$ (**3**): it was essential to perform crystallization relatively quickly, unlike for the preparation of complex **1** (see Experimental section) and from this view the array possibly illustrates an initial nucleation step in the system.

The 2D subtopologies in **2** and **3** are related to the non-covalent (3,6)-networks (CH · · · N) of 1,3,5-tricyanobenzene and similar 3 + 3 self-complementary molecules of trigonal symmetry,[17] but are quite remarkable for coordination polymers.[18] Each tricopper unit coordinates three distal axial chloride (bromide) ions, one of them bridging between two clusters and this results in association of the metal–organic subtopologies into double layers at 4.78 Å. That the tricopper clusters retain an electrophilic character at the opposite axial side was best reflected by immobilization of an additional bitriazole molecule that fits comfortably inside the cone-shaped binding pocket (geometrically similar to that of boron subphthalocyanines)[19] and interacts with two copper atoms simultaneously (Fig. 5), which is prototypal for accommodation of guest molecules by multiple interactions. The additional btr molecules, as pillar modules, extend the chloride (bromide) bridged double layers into the 3D framework. Considering these additional btr and chloride (bromide) bridges, the overall 3D topology may be regarded as an eight-connected primitive hexagonal net (Schläfli symbol $\{3^6;4^{18};5^3;6\}$).

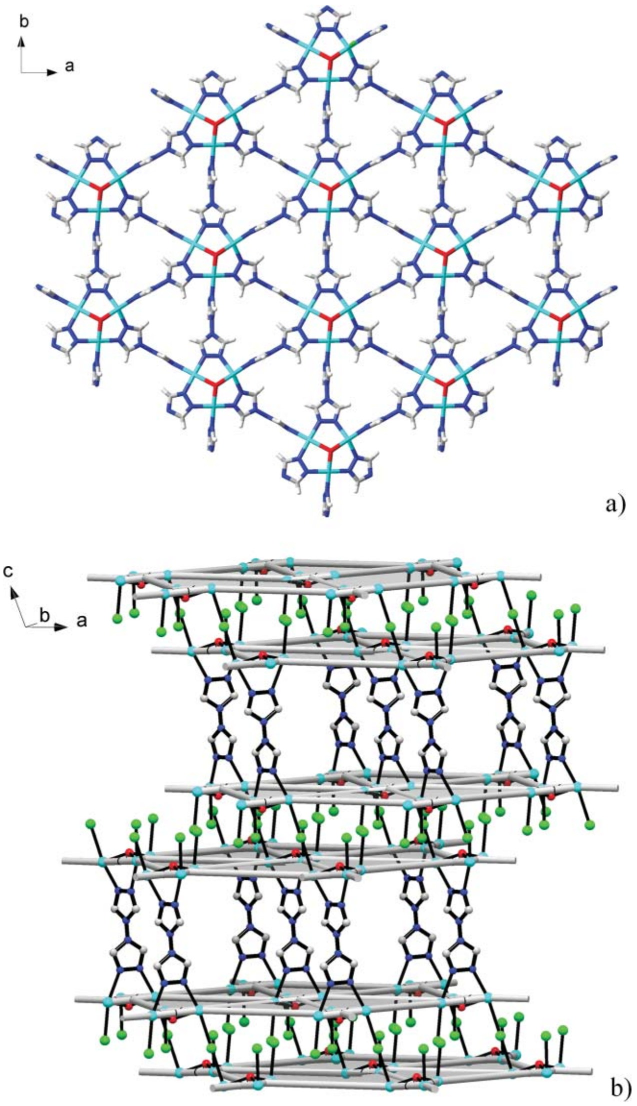

Fig. 4 a) Six-connected 2D coordination subtopology in **2** and **3** originating in association of self-complementary units; b) the entire 3D structure is sustained by cross-linking of the 2D subtopologies.

Conclusion

Our study demonstrates an efficient protocol for the integration of polynuclear ensembles into extended arrays and the pathway, in which the $Cu_3(\mu_3\text{-}OH)$ core is applicable as a secondary building block, for the generation of coordination frameworks. The results, which are reported here, provide an attractive prototype for the development of frameworks with multiple guest-binding sites using general principles of crystal design and we are currently exploring incorporation of the $Cu_3(\mu_3\text{-}OH)$ clusters into porous metal–organic structures.

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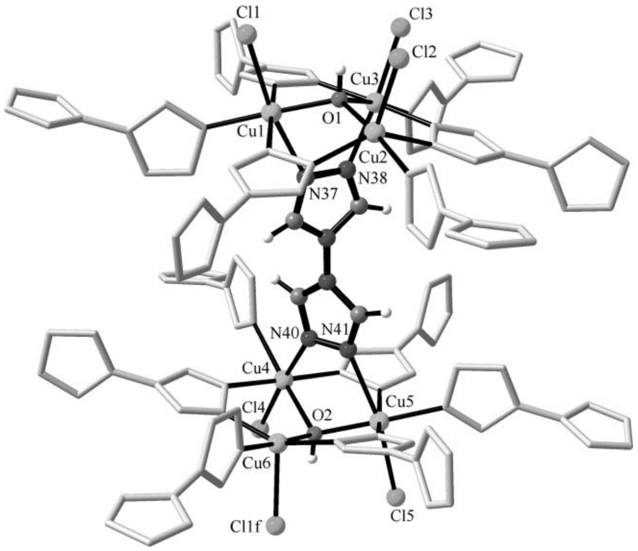

Fig. 5 Illustration of how the pair of tricopper clusters in **3** provides accomodation of an additional btr molecule by multiple coordination bonding. Note the presence of six- and five-coordinated copper ions [Cu(2) and Cu(6)].

Experimental

4,4′-Bi(1,2,4-triazole) was prepared in 58% yield by reacting 4-amino-4*H*-1,2,4-triazole and dimethylformamide azine using the literature method.[20] Examination of the reaction of bitriazole ligand towards copper(II) chloride (bromide) in aqueous or aqueous alcohol media reveals that formation of μ_3-hydroxotricopper(II) clusters dominates the structure of the products and is a suitably predictable feature of the system.

Syntheses

Synthesis of 1 and 2. Slow interdiffusion of solutions of $CuCl_2 \cdot 2H_2O$ (34.0 mg, 0.20 mmol) in 3 mL methanol and btr (27.2 mg, 0.20 mmol) in 1 mL water affords, over a period of 9–10 d, large green octahedra of complex **1** in 60% yield, as a mixture with a minor product, $Cu_3Cl_6(btr)_4$ (blue plates, *ca.* 10%). When $CuBr_2$ (22.3 mg, 0.10 mmol) was used instead of the chloride, the reaction led to complex **2** (40%). Well-developed crystals of **2** were grown using a solution of $CuBr_2$ in ethanol. Anal. for **1**, $C_{12}H_{24}Cl_7Cu_6N_{18}O_{8.5}$. Calc. (%): C, 12.15; H, 2.04; N, 21.27. Found (%): C, 12.04; H, 1.92; N, 21.06. For **2**, $C_{28}H_{42}Br_{10}Cu_6N_{42}O_8$. Calc. (%): C, 14.78; H, 1.86; N, 25.86. Found (%): C, 14.49; H, 1.91; N, 25.74.

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

Synthesis of 3. Diethyl ether–THF (1 : 1) vapor diffusion into a solution of $CuCl_2 \cdot 2H_2O$ (17.0 mg, 0.10 mmol) and btr (13.6 mg, 0.10 mmol) in 1 mL water for 10–12 h affords green crystals of the complex in 90% yield. Anal. for **3**, $C_{28}H_{46}Cl_{10}Cu_6N_{42}O_{10}$. Calc. (%): C, 18.01; H, 2.48; N, 31.52. Found (%): C, 17.86; H, 2.34; N, 31.12.

X-Ray crystallography

Crystallographic measurements were made at 213 K using a Stoe Imaging Plate Diffraction System with Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods using the program SHELXS-97.[21] The refinement and all further calculations were carried out using SHELXL-97.[21] The non-H atoms were refined anisotropically, using weighted full-matrix least-squares of F^2 (Table 2). CH and μ_3-OH hydrogen atoms were added geometrically. Since structure **1** comprises symmetry related hydroxo- and oxotricopper clusters, the OH hydrogen atom is disordered over two structurally equal μ_3-O fragments, and it was added with partial occupancy factor 0.5. Three non-coordinated chloride ions in the structure of **3** were unequally disordered over closely situated positions and only the major contributions were refined anisotropically. In structure **2**, the μ_4-btr ligand is disordered between two symmetry related overlapping positions,

Table 2 Crystal data for $[\{Cu_3(\mu_3\text{-}OH)\}\{Cu_3(\mu_3\text{-}O)\}(\mu_4\text{-}btr)_3(H_2O)_4(OH)_2Cl_6]Cl \cdot 0.5H_2O$ (**1**), $[\{Cu_3(\mu_3\text{-}OH)\}_2(\mu_3\text{-}btr)_6(\mu_4\text{-}btr)(\mu\text{-}Br)Br_4]Br_5 \cdot 6H_2O$ (**2**) and $[\{Cu_3(\mu_3\text{-}OH)\}_2(\mu_3\text{-}btr)_6(\mu_4\text{-}btr)(\mu\text{-}Cl)Cl_4]Cl_5 \cdot 8H_2O$ (**3**)

	1	2	3
Formula	$C_{12}H_{24}Cl_7Cu_6N_{18}O_{8.50}$	$C_{28}H_{42}Br_{10}Cu_6N_{42}O_8$	$C_{28}H_{46}Cl_{10}Cu_6N_{42}O_{10}$
M	1185.88	2275.38	1866.81
Crystal system	Cubic	Monoclinic	Monoclinic
Space group, *Z*	$Fd\bar{3}c$, 32	$C2/m$, 2	Cc, 4
a/Å	30.0968(12)	11.9996(11)	21.359(2)
b/Å		21.067(2)	12.0195(8)
c/Å		15.648(2)	28.954(2)
β/°		109.55(1)	97.90(1)
U/Å^3	27262(2)	3727.4(6)	7362.8(10)
μ(Mo-Kα)/cm^{-1}	42.97	71.10	21.38
D_c/g cm^{-3}	2.311	2.027	1.684
$2\theta_{max}$/°	51.8	53.5	53.5
Measured/unique reflns	8263/1078	11860/3893	17532/12531
Parameters refined	81	237	846
$R1$, $wR2$ ($I > 2\sigma(I)$)	0.048, 0.144	0.049, 0.106	0.076, 0.198[a]
$R1$, $wR2$ (all data)	0.054, 0.147	0.082, 0.112	0.084, 0.202
Max, min peak/e Å^{-3}	1.37, −0.89	1.00, −1.28	1.42, −0.84

[a] Flack parameter x = 0.04(2).

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as donor of four Cu–N bonds towards a pair of tricopper clusters and this disorded was refined without constraints in geometry (alternative refinements of the structure either in space groups *C*2 or *Cm* did not lead to a ordered model). Some of the non-coordinated bromide ions and water molecules in this structure are badly disordered and the remaining electron density was modeled using Squeeze.[13] Graphical visualisation of the structures was made using the program Diamond.[22]

CCDC reference numbers 600030–600032.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b604804h

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