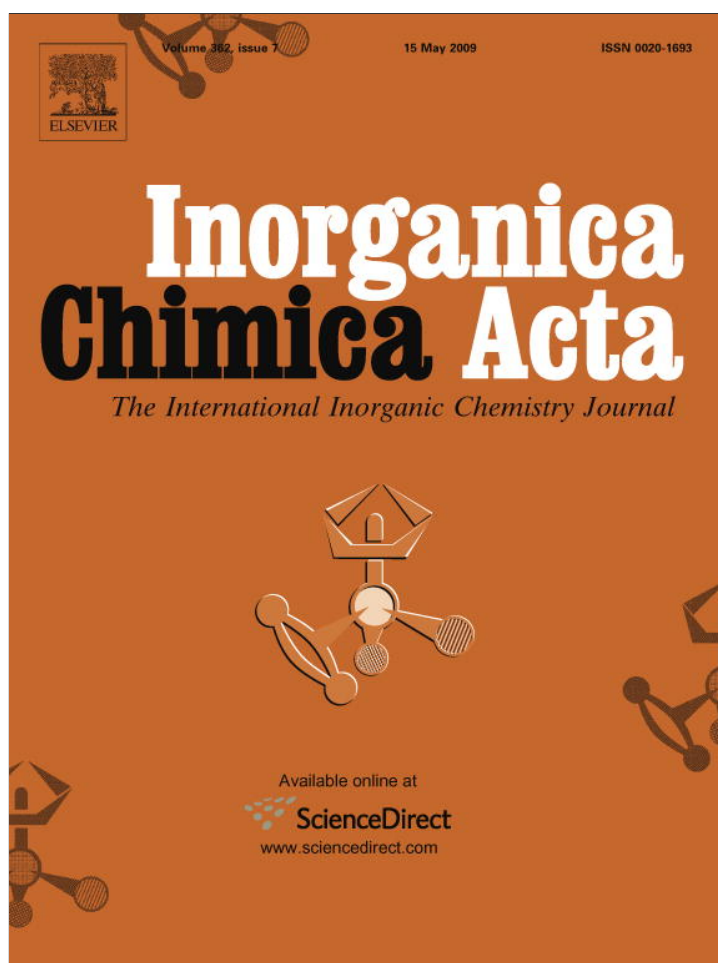


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Magnetic and luminescence properties of Cu(II), Cu(II)₄O₄ core, and Cd(II) mixed-ligand metal–organic frameworks constructed from 1,2-bis(1,2,4-triazol-4-yl)ethane and benzene-1,3,5-tricarboxylate

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ABSTRACT

The hydrothermal reaction of Cu(NO₃)₂ · 3H₂O, Cu(ClO₄)₂ · 6H₂O, or CdSO₄ · 8/3H₂O with benzene-1,3,5-tricarboxylic acid (H₃btc) and 1,2-bis(1,2,4-triazol-4-yl)ethane (btre) produced the mixed-ligand coordination polymers and networks (MOFs) $^1_{\infty}\{[\text{Cu}(\text{H}_2\text{btc})_2(\mu\text{-btre})]\}$ (**1**), $^3_{\infty}\{[\text{Cu}_4(\mu_5\text{-btc})_2(\mu_3\text{-OH})_2(\mu_4\text{-btre})] \cdot 2\text{H}_2\text{O}\}$ (**2**), and $^3_{\infty}\{[\text{Cd}_3(\mu_6\text{-btc})_2(\mu_4\text{-btre})] \cdot \text{H}_2\text{O}\}$ (**3**). The centrosymmetric tetranuclear, chair-shaped or stepped-cubane Cu₄O₄ metal building unit in **2** has three different Cu contacts, each involving more than one bridging group. A quasi-butterfly magnetostructural model shows dominant antiferromagnetic interactions in this Cu₄ unit with three different magnetic exchange pathways with $2J_1 = 258$, $2J_2 = -416$, and $2J_3 = 484 \text{ cm}^{-1}$ from the magnetic susceptibility measurement between 1.9 and 300 K. For this Cu₄O₄ unit the Eigenvalues associated with the zero field spin Hamiltonian were calculated by solving the 16×16 matrix in order to obtain here the numerical expression for the magnetic susceptibility. The cadmium-btre framework **3**, with bridged Cd strands, shows a strong bluish fluorescence at 421 nm upon excitation at 317 nm (not seen in the free btre ligand).

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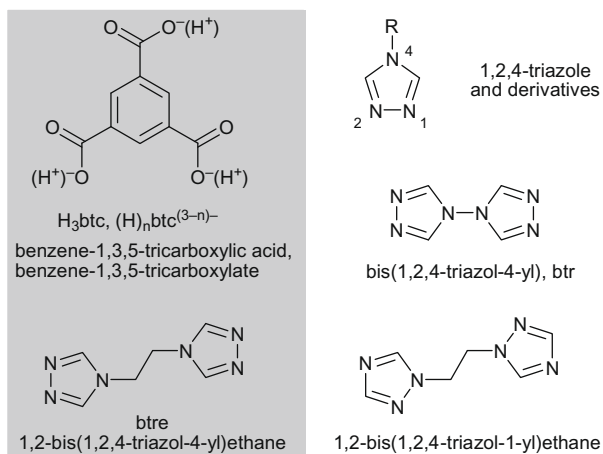
1. Introduction

Metal–organic networks, such as coordination polymers or metal–organic frameworks (MOFs) are of timely interest due to their topologies and application oriented properties such as gas adsorption, separation, luminescence, nonlinear optics, magnetism, ion exchange, and catalysis [1–4]. In this field mixed-ligand networks have become more important recently [5–9]. Multi-carboxylate ligands, especially benzoic acid-based ligands [8,10], and 1,2,4-triazole derivatives [9,11] are frequent choices for metal–organic networks [1–7]. Benzene-1,3,5-tricarboxylate is a rigid, planar molecule and has been extensively used in the form of its three anions H_nbtc⁽³⁻ⁿ⁾⁻ ($n = 0, 1, 2$) (Scheme 1) as a bridging ligand in the synthesis of multi-dimensional MOFs. Recent examples [12] (metals as cations and ligand bridging mode in parentheses) are for H₂btc⁻ (Mn-μ₂) [13], for Hbtc²⁻ (Mn-μ₂ [14], Mn-μ₃ [14,15], Co-μ₂ [16], Co-μ₃ [14,15], Ni-μ₃ [17], Cu-μ₂ [18], Zn-μ₂ [14,15,19], Zn-μ₃ and -μ₄ [15], Cd-μ₃ [20]) and for btc³⁻, (Fe-μ_{2,3} [21], Co-μ₂ [22,23], Co-μ₃ [23,24], Ni-μ₂ [22,25], Ni-μ₃ [26,27], Cu-μ_{2,3} [28], Cu-μ₃ [29], Zn-μ₃ [27,30], Ag-μ₃ [31], Ag-μ_{5,6} [32], In-μ₃ [33], Y-μ₂ [34]). The 1,2,4-triazole ligand and its 4-substi-

tuted derivatives can be used to obtain linear coordination polymers based on its bridging function, e.g. with Cu²⁺ [35], Zn²⁺ [36], Cd²⁺ [37], together with a wide variety of molecular polynuclear complexes [38]. The N1:N2-bridging mode of 1,2,4-triazole or triazolate (Scheme 1) constitutes a short ligand bridge between metal atoms which is a prerequisite for stronger magnetic coupling between paramagnetic metal centers [1]. Surprisingly, with the related 4,4'-bis(1,2,4-triazol-4-yl) ligand (abbreviated as btr) this N1:N2-bridging coordination mode has only been observed recently with Cu(II) [12,39]. Typically the btr ligand links transition metal(II) ions using only one nitrogen atom from each 1,2,4-triazole ring (κN1:N1' bridge) – resulting in one-, [40,41], two-, and three-dimensional networks [42–44]. When spacers like methylene groups are introduced between the two 1,2,4-triazole rings, the resulting ligand acquires more flexibility. Therefore, we selected 1,2-bis(1,2,4-triazol-4-yl)ethane (abbreviated as btre) [45]. This btre ligand must not be mistaken with the more widely employed 1,2-bis(1,2,4-triazol-1-yl)ethane [46] and other ~alkane ligands (Scheme 1) [47]. These related 1,2-bis(1,2,4-triazol-1-yl) ligands do only bridge between two metal atoms in a κN4:N4' mode. Hence, they cannot bring two metal atoms closely together as the btre ligand can through its κN1:N2 bridge. The btre ligand has been scarcely used in metal–complex or –organic network synthesis. A CSD search [12] gave $^2_{\infty}\{[\text{M}(\text{NCS})_2(\mu_2\text{-btre-}\kappa^2\text{N1:N1}')_2(\text{NCS})_2]\}$ (M = Fe, Co) [48], and $^3_{\infty}\{[\text{Cu}_3(\mu_4\text{-btre-}\kappa^4\text{N1:N2:N1':N2'})_2\text{-}$

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Scheme 1. Ligands relevant to this work. The grey underlined ligands are synthetically used in this work.

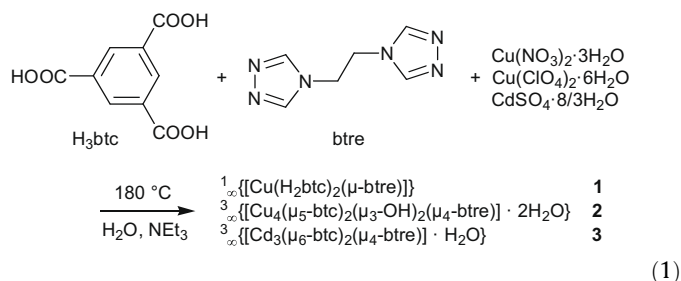
(μ_3 -btre- κ^3 N1:N2:N1') $_4$ (H₂O) $_2$] $_2$ (ClO₄) $_{12}$ · 2H₂O} [49] as the only examples. We have recently added mixed-ligand 3D coordination networks of btre with benzene-1,3,5-tricarboxylate and Ni(II) or Zn(II) as metal atoms which feature solid-state crystal-to-crystal transitions upon drying (Ni, Zn), luminescence (Zn) or antiferromagnetic (Ni) coupling. The interesting btre coordination mode is μ_4 -btre- κ^4 N1:N2:N1':N2' where the bis-triazole-type ligand bridges between four metal atoms occupying all of its sp²-hybridized nitrogen atoms and bringing two metal atoms in vicinity through the κ N1:N2 bridge [5].

Herein, we report the syntheses, structures, magnetic (for **2**), and luminescence (for **3**) properties of the mixed-ligand coordination networks with the btre ligand: $^1_{\infty}$ {[Cu(H₂btc)₂(μ -btre)]} (**1**), $^3_{\infty}$ {[Cu₄(μ_5 -btc)₂(μ_3 -OH)₂(μ_4 -btre)] · 2H₂O} (**2**) and $^3_{\infty}$ {[Cd₃(μ_6 -btc)₂(μ_4 -btre)] · H₂O} (**3**).

2. Results and discussion

2.1. Syntheses

Hydrothermal treatments of different metal salts with 1,2-bis(1,2,4-triazol-4-yl)ethane (btre) and benzene-1,3,5-tricarboxylic acid (H₃btc) yield mixed-ligand coordination polymers (Eq. (1)). Complete deprotonation of H₃btc is achieved through the addition of triethylamine (NEt₃) for **2** and **3**.



The vibrational modes for carboxylate groups, substituted benzene, and triazole rings confirm the presence of (partly) deprotonated btc and btre ligands in compounds **1–3**. An absorption band at 1700 cm⁻¹ in compound **1** indicates the presence of free -COOH groups. The absence of bands at 1730–1690 cm⁻¹ for -COOH is indicative of fully deprotonated btc³⁻ ligands in compounds **2** and **3** [50]. The extensive hydrogen-bonding network present in the crystal structures is indicated through the δ - and γ -vibrational modes between 880 and 1350 cm⁻¹ (see Section 4) [51].

2.2. Thermal stability

Degradation of the organic parts of the mixed-ligand networks **1–3** starts above 250 °C according to thermogravimetric analyses (Figs. S1–S3 in Supporting information). Compound **1** shows a weight loss from 100 to 365 °C which corresponds to the loss of one H₃btc and one btre ligand (observed 57.0, calc. 57.9%). A further gradual weight loss occurs until 600 °C with a remaining weight of 32.7%. Compound **2** shows a weight loss from 110 to 280 °C which corresponds to the loss of the water of crystallization (obs. 3.9, calc. 4.0%). The second weight loss is observed in the range 290–350 °C which assigned to the removal of one btre ligand and six CO molecules from the two btc ligands (obs. 38.0, calc. 38.3%). A further gradual weight loss occurs until 600 °C with a remaining weight of 43.6%. Compound **3** is stable up to 230 °C. The first weight loss in the temperature range 250–270 °C for **3** corresponds to the removal of the crystal water molecule (obs. 3.7, calc. 1.9%). A second weight loss in the range 380–460 °C is assigned to the removal of one btre and one btc ligand (or its decomposition products, obs. 38.0, calc. 37.0%). A continuing weight loss until 600 °C matches with the loss of the organic moiety.

2.3. Crystal structure of $^1_{\infty}$ {[Cu(H₂btc)₂(μ -btre)]}, **1**

The copper atom in **1** coincides with an inversion center and is *trans* coordinated by two nitrogen atoms from two bridging btre ligands (κ N1:N1' mode) and two carboxylate oxygen atoms of two terminal H₂btc groups, respectively (Fig. 1). This square planar Cu–N₂O₂ coordination is supplemented by two longer Jahn-Teller-distorted Cu...O contacts to oxygen atoms of pseudo-chelating carboxylate groups. The 1D-Cu(μ -btre)-strands extend along the (1 1 0)-plane. The strands are interconnected through hydrogen bonds from one carboxyl group of H₂btc to the carboxylate (Fig. 2) and through complementary H bonds between two carboxyl groups.

2.4. Crystal structure of $^3_{\infty}$ {[Cu₄(μ_5 -btc)₂(μ_3 -OH)₂(μ_4 -btre)] · 2H₂O} **2**

Compound **2** features a centrosymmetric tetranuclear metal unit with two crystallographically different copper atoms (Fig. 3).

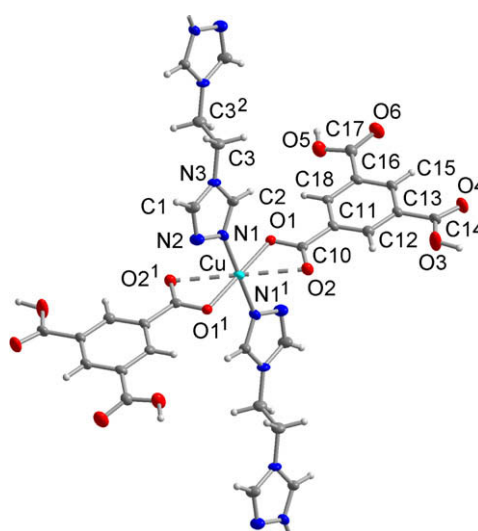


Fig. 1. Coordination environment around Cu in **1**. Selected distances [Å] and angles [°]: Cu–O1 1.967(3), Cu–N1 1.985(4), Cu–O2 2.569(3), O1–Cu–O1' 180.0, O1–Cu–N1' 91.3(1), O1–Cu–N1 88.7(1), O1–Cu–O2 56.4(1), N1–Cu–N1' 180.0, O1–Cu–O2 123.6(1), N1–Cu–O2 83.3(1), N1–Cu–O2 96.7(1), O1–Cu–O2 123.6(1), O1–Cu–O2 56.4(1), N1–Cu–O2 96.7(1), N1–Cu–O2 83.3(1), O2–Cu–O2' 180.0. Symmetry codes 1 = -x, -y, -z; 2 = -1 - x, 1 - y, -z.

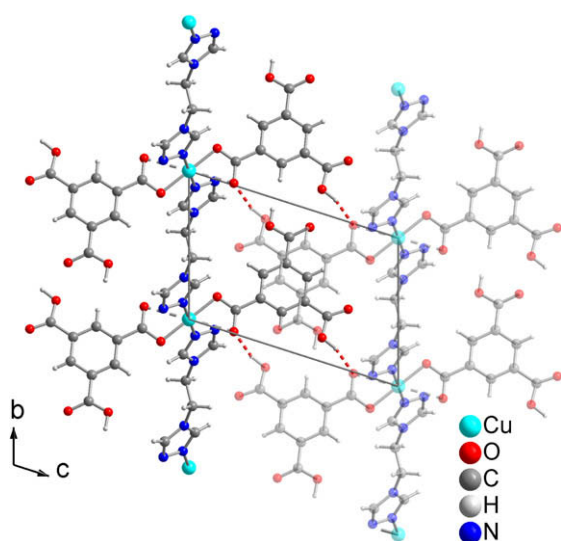


Fig. 2. Packing diagram of **1** showing two $\{Cu(H_2btc)_2\}(\mu\text{-btre})$ strands with one of them semi-transparent for clarity to illustrate that the H_2btc^- ligand does not function as a bridge between the Cu atoms. Hydrogen-bonding interactions (dashed line) as O–H, H \cdots O, O \cdots O, O–H \cdots O (\AA , $^\circ$) 0.95(6), 1.67(6), 2.601(5), 163(5) (to carboxylate shown above); 0.96(4) 1.62(4) 2.579(5) 176(5) (complementary H-bond between carboxyl groups, not shown).

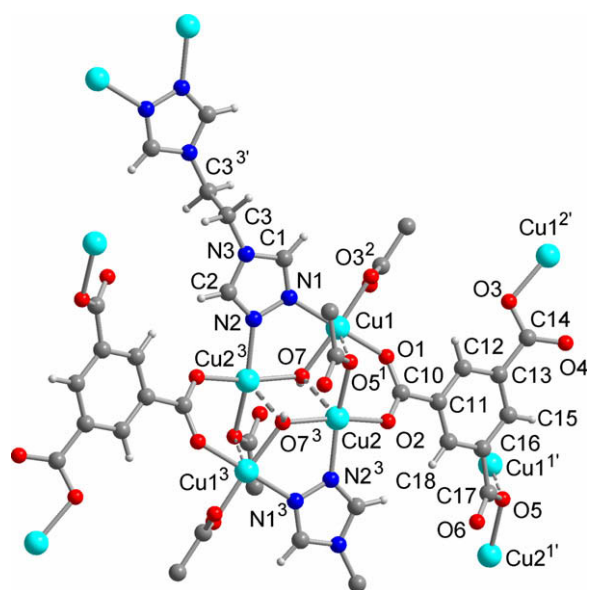


Fig. 3. Coordination environment of the Cu_4 core in **2**. Selected distances [\AA] and angles [$^\circ$]: Cu1–O1 1.919(3), Cu1–O3² 1.941(3), Cu1–O5¹ 2.476(3), Cu1–O7 1.929(3), Cu1–N1 1.965(3), Cu2–O2 1.945(3), Cu2–O5¹ 2.035(3), Cu2–O7 2.270(3), Cu2–O7³ 1.931(3), Cu2–N2³ 2.011(3), O1–Cu1–O7 93.5(1), Cu1 \cdots Cu2 3.1677(7), Cu2 \cdots Cu2³ 3.1428(7), Cu1 \cdots Cu2³ 3.4035(7) O1–Cu1–O3² 87.8(1), O1–Cu1–N1 177.6(1), O7–Cu1–O3² 172.9(1), O7–Cu1–N1 87.3(1), O3²–Cu1–N1 91.6(1), O7³–Cu2–O2 169.4(1), O7³–Cu2–N2³ 86.0(1), O7³–Cu2–O5¹ 92.9(1), O7³–Cu2–O7 83.5(1), O2–Cu2–N2³ 85.1(1), O2–Cu2–O5¹ 97.2(1), O2–Cu2–O7 94.8(1), N2³–Cu2–O5¹ 164.5(1), N2³–Cu2–O7 113.4(1), O5¹–Cu2–O7 81.8(1), Cu1–O5¹–Cu2 88.6(1), Cu1–O7–Cu2 97.6(1), Cu1–O7–Cu2³ 123.7(1), Cu2–O7–Cu2³ 96.5(1). Symmetry codes: 1 = x , 1 + y , z ; 1' = x , $-1 + y$, z ; 2 = $-x$, 0.5 + y , 0.5 – z ; 2' = $-x$, $-0.5 + y$, 0.5 – z ; 3 = $1 - x$, $1 - y$, $1 - z$.

The atoms in the Cu_4 core are bridged by two btre-ligands in $\kappa N1:N2$ mode, by two μ_3 -hydroxo groups, by two μ_2 -*syn-syn* carboxylate groups in $\kappa O'O'$ mode and by two μ_2 -O atoms of carboxylate groups in $\kappa O:O$ mode. Each square-pyramidal Cu atom (Cu1 τ = 0.08, Cu2 τ = 0.08) [52] is thus coordinated by three O and

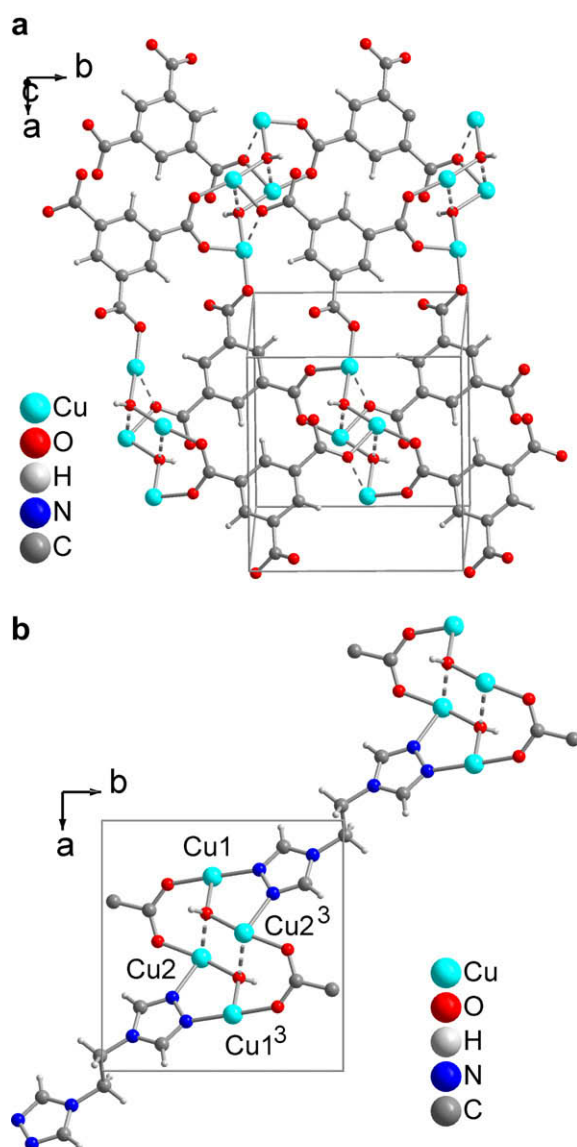


Fig. 4. Packing analysis for **2** by differentiation in individual (a) $\{Cu\text{-OH}/btc\}$ -nets and (b) Cu-btre-units. Symmetry code: 3 = $1 - x$, $1 - y$, $1 - z$.

one N atom in the basal plane plus an apical O atom with a slightly longer Cu–O bond. Each btre ligand bridges between four and each btc^{3-} ligand between five copper atoms (Fig. 3).

The Cu atoms, the OH and btc ligands in **2** form double layers parallel to the (-204) plane (Fig. 4a). These layers are connected through the btre ligands (Fig. 4b) to give a dense packed 3D structure with narrow channels (along b , Fig. S4 in Supporting information) which are occupied by water molecules of crystallization.

2.5. Crystal structure of ${}^3_\infty\{[Cd_3(\mu_6\text{-btc})_2(\mu_4\text{-btre})] \cdot H_2O\}$, **3**

Compound **3** features a cadmium strand with two crystallographically different cadmium sites (Fig. 5). The neighboring Cd1 and Cd2 atoms are bridged by one triazole and two btc groups. The adjacent symmetry related Cd1 atoms are bridged by two carboxylate groups. Atom Cd1 is six- to seven-coordinated [53] with 5–6 oxygen atoms from four btc ligands, 1–2 of them chelating and one btre-nitrogen atom. The Cd1–O13^{1''} bond is slightly longer

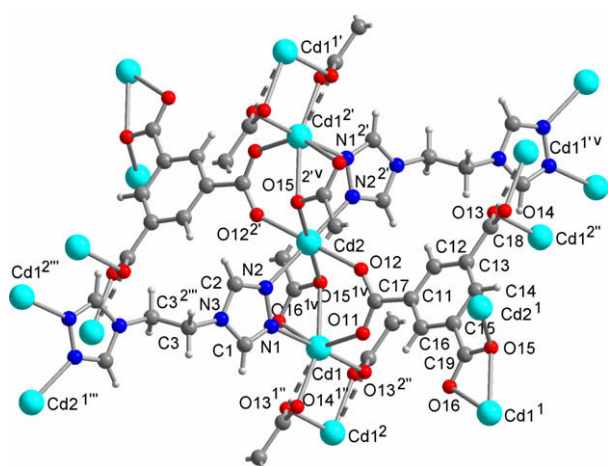


Fig. 5. Coordination environment of the cadmium strand in **3**. Selected distances [Å] and angles [°]: Cd1–O11 2.320(2), Cd1–O13^{1v} 2.777(2), Cd1–O13^{2v} 2.244(2), Cd1–O14^{1v} 2.325(2), Cd1–O15^{1v} 2.4585(18), Cd1–O16^{1v} 2.469(2), Cd1–N1 2.309(2), Cd2–O12 2.205(2), Cd2–O15^{1v} 2.315(2), Cd2–N2 2.305(2), O13^{2v}–Cd1–N1 176.69(7), O13^{2v}–Cd1–O11 91.23(7), N1–Cd1–O11 87.88(7), O13^{2v}–Cd1–O14^{1v} 95.69(7), N1–Cd1–O14^{1v} 81.33(7), O11–Cd1–O14^{1v} 99.72(7), O13^{2v}–Cd1–O15^{1v} 96.79(6), N1–Cd1–O15^{1v} 86.43(7), O11–Cd1–O15^{1v} 92.22(6), O14^{1v}–Cd1–O15^{1v} 162.51(7), O13^{2v}–Cd1–O16^{1v} 96.55(7), N1–Cd1–O16^{1v} 85.98(7), O11–Cd1–O16^{1v} 144.96(6), O14^{1v}–Cd1–O16^{1v} 113.34(7), O15^{1v}–Cd1–O16^{1v} 53.00(6), O12–Cd2–N2 98.06(8), O12–Cd2–N2^{2v} 81.94(8), O12–Cd2–O15^{1v} 83.43(7), O12–Cd2–O15^{2v} 96.57(7), N2–Cd2–O15^{1v} 86.34(7), N2–Cd2–O15^{2v} 93.66(7). Symmetry codes: 1 = 1 + x, 1 + y, z; 1' = 1 + x, y, 1 + z; 1'' = -1 + x, -1 + y, -1 + z; 1''' = x, -1 + y, -1 + z; 1^v = 1 + x, 1 + y, 1 + z; 1^v' = -1 + x, -1 + y, z; 2 = -x, -y, -z; 2' = 1 - x, -y, 1 - z; 2'' = 1 - x, 1 - y, 1 - z; 2''' = 1 - x, -1 - y, -z; 2^v = 2 - x, 1 - y, 1 - z.

than the others to yield a semi-chelating and bridging carboxylate $\kappa^3O^v:O^{v'}:O^{v''}$ unit. The octahedral coordination sphere of the inversion symmetric Cd2 consists of four oxygen atoms from four btc ligands and two *trans*-btre nitrogen atoms. Each btre ligand connects four cadmium atoms and each btc³⁻ ligand bridges between six cadmium atoms in a $\kappa^6O^v:O^{v'}:O^{v''}:O^{v'''}:O^{v''''}:O^{v''''}$ mode (Fig. 5).

The Cd1 atoms and the btc ligands alone form double layers parallel to the (-110) plane along the *ab* diagonal (Fig. 6a). These double layers are connected through the Cd2 atoms and the btre ligands to a densely packed 3D framework (Fig. 6b). Voids in the double layers (Fig. 6a) are filled by the bridging btre ligands and disordered water of crystallization (not shown) (Fig. 6b). The {Cd–btre}-substructure are parallel strands (Fig. 6c). Compound **3** is isostructural to ${}^3\infty\{[\text{Zn}_3(\mu_6\text{-btc})_2(\mu_4\text{-btre})] \cdot \sim 0.67\text{H}_2\text{O}\}$ which was obtained from a solid-state single crystal-to-crystal transition of ${}^3\infty\{[\text{Zn}_3(\mu_4\text{-btc})_2(\mu_4\text{-btre})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\}$ [5].

2.6. Magnetic properties of **2**

The thermal dependence of $\chi_M T$ of compound **2** in the temperature range 1.9–300 K is depicted in Fig. 7 (χ_M being the magnetic susceptibility per mol of Cu₄). The $\chi_M T$ value at room temperature is 0.84 cm³ mol⁻¹ K and it decreases continuously from room temperature to 1.9 K.

This decrease is very pronounced at high temperatures, but becomes very slow below 100 K. These features are indicative of a dominant antiferromagnetic interaction that allows **2** to reach an *S* = 0 ground spin state that is completely populated at low temperatures. Compound **2** has a tetranuclear, chair-shaped or stepped-cubane Cu₄O₄ core [54,55] for which three different magnetic exchange pathways can be observed (Scheme 2). $2J_1$, $2J_2$, and $2J_3$ correspond to the magnetic coupling constant between Cu2...Cu2', Cu1...Cu2', and Cu1...Cu2, respectively.

Such a coupling scheme has been observed in complexes with a Cu₄O₄ defective double cubane structure, but usually those sys-

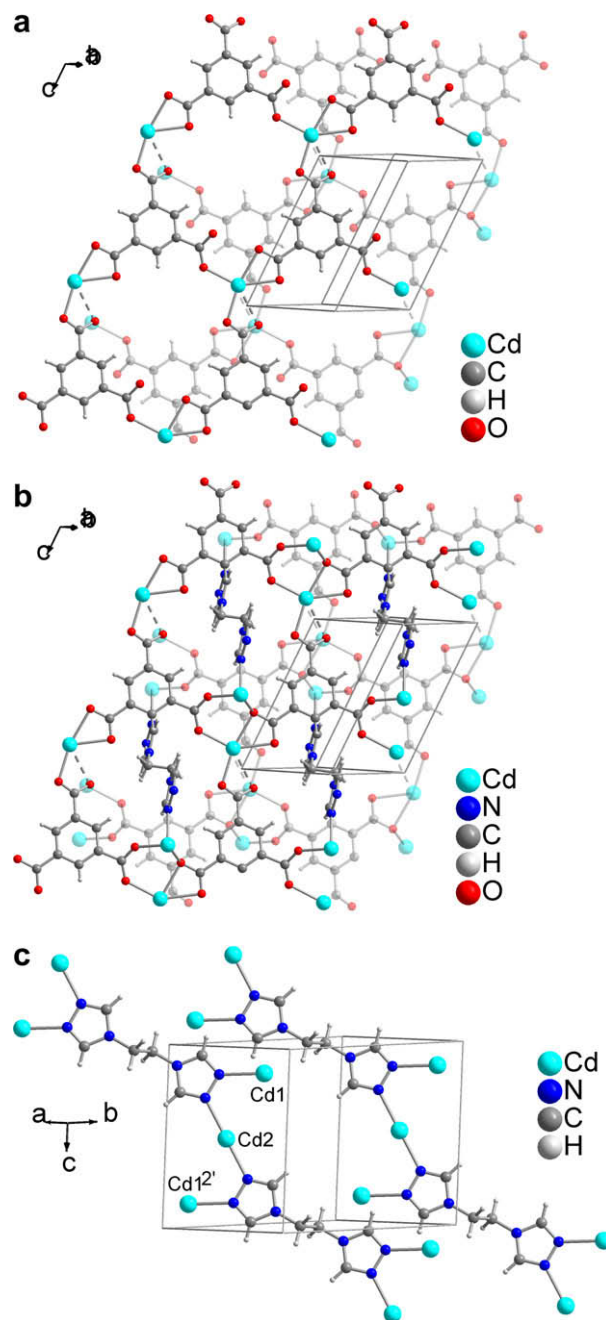


Fig. 6. Packing analysis for **3** by differentiation in individual (a) {Cd1–btc}-double layers and (b) {Cd1–btc}-double layers with Cd2 atoms and btre ligands which will then link these double layers. For clarity only one double layer is shown in (a) and (b). The rear part of the double layer is depicted semi-transparent. (c) {Cd–btre}-strands. Symmetry label: 2' = 1 - x, -y, 1 - z.

tems have higher symmetry and the number of coupling constants can be reduced so that the system can easily be solved [56–58]. In other “Cu₄” structures the system follows a dinuclear model and the Bleaney–Bowers [57,59] equation can be used to obtain the values of the coupling constants [54,60]. In a molecular tetranuclear copper(II) compound with a chair-shaped Cu₄O₄ core Gou et al. describe the magnetic properties with an identical magnetic coupling scheme [55]. They perform an interesting variable reorganization that allows them to obtain the Eigenvalues of the system, however, the magnetic susceptibility equation is not easily deduced from their analysis. We present herein a full description of the magnetic study and a simple equation for the magnetic susceptibility in the Cu₄O₄-core compound **2** for which three exchange

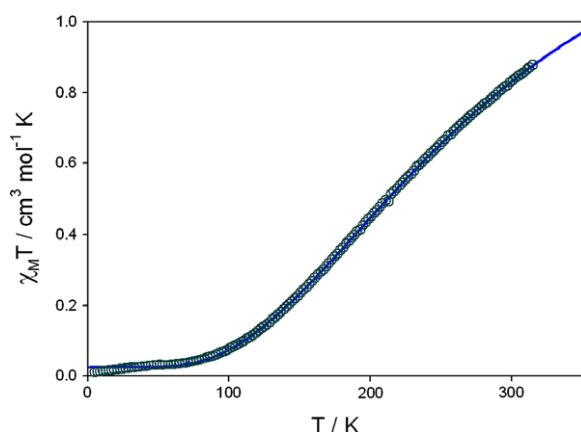
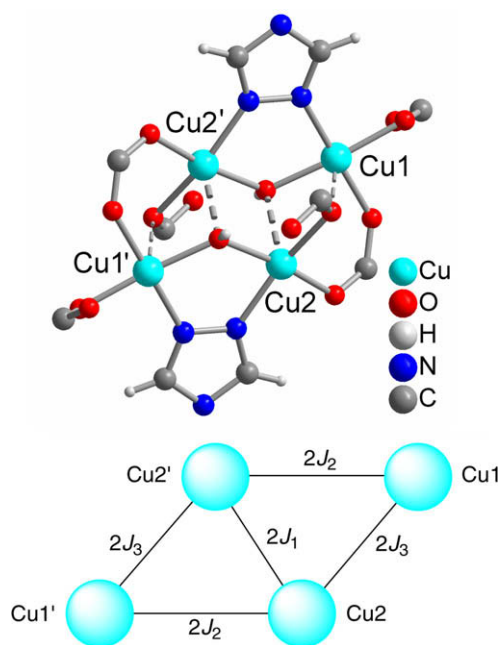


Fig. 7. Thermal dependence of the χ_{MT} for compound **2**. The solid line is the best fit to Eq. (3), see text.



Scheme 2. Cu_4O_4 core unit and magnetic coupling scheme for compound **2**.

pathways are active and very different. An additional feature in **2** is that each magnetic exchange pathway involves more than one bridging group: $2J_1$ a double μ -oxo bridge, $2J_2$ a μ -oxo and an N1:N2 - triazole bridge and $2J_3$ a μ -oxo from a hydroxo group, a μ -oxo from a carboxylate group and a *syn-syn* carboxylate group. The zero field spin Hamiltonian for such a system is then given by Eq. (2).

$$\hat{H} = -2J_1(\hat{S}_1\hat{S}_2) - 2J_2(\hat{S}_1\hat{S}_3 + \hat{S}_2\hat{S}_4) - 2J_3(\hat{S}_1\hat{S}_4 + \hat{S}_2\hat{S}_3) \quad (2)$$

This Hamiltonian gives rise to six spin states corresponding to the total spin operators 2, 1, and 0. Due to its low symmetry Kambe's vector coupling scheme does not allow to obtain the Eigenvalues associated with that Hamiltonian, so they have been obtained by solving the 16×16 matrix and they are listed in Table 1. The magnetic susceptibility expression, Eq. (3) is calculated from the Heisenberg–Dirac–van Vleck equation.

$$\chi = \frac{2N\beta^2 g^2}{kT} \left[\frac{5e^{-\alpha/kT} + e^{-\epsilon/kT} + e^{-\gamma/kT} + e^{-\delta/kT}}{5e^{-\alpha/kT} + 3e^{-\epsilon/kT} + 3e^{-\gamma/kT} + 3e^{-\delta/kT} + e^{-\eta/kT} + e^{-\omega/kT}} \right] \quad (3)$$

Table 1

Eigenvalues associated with the total spins for **2**.

S_T	E	Eigenvalues
2	α	$-(J_1/2) - J_2 - J_3$
1	ϵ	$-(J_1/2) + J_2 + J_3$
1	γ	$(J_1/2) + \sqrt{J_1^2 + J_2^2 + J_3^2 + 2J_2J_3}$
1	δ	$(J_1/2) - \sqrt{J_1^2 + J_2^2 + J_3^2 + 2J_2J_3}$
0	η	$(J_1/2) + J_2 + J_3 + \sqrt{J_1^2 - 2J_1J_2 + 4J_2^2 - 2J_1J_3 - 4J_2J_3 + 4J_3^2}$
0	ω	$(J_1/2) + J_2 + J_3 - \sqrt{J_1^2 - 2J_1J_2 + 4J_2^2 - 2J_1J_3 - 4J_2J_3 + 4J_3^2}$

N stands for the Avogadro's number, g the Landé factor, β the Bohr magneton, k Boltzmann's constant and $\alpha - \omega$ for the Eigenvalues given in Table 1. We have checked that expression (3) can also be deduced by the simplification of the model developed by Hatfield and co-workers for the general copper(II) tetramer with C_2 symmetry [61]. Best least-square fit of the magnetic susceptibility data of compound **2** to Eq. (3) gave the parameters: $g = 2.00$, $2J_1 = 258$, $2J_2 = -416$, $2J_3 = 484 \text{ cm}^{-1}$, and $R = 0.99995$. These coupling constants would lead to this spin organization ($\uparrow\downarrow\uparrow$) with an $S = 0$ ground spin state in which $2J_1$ is frustrated and the system dominated by $2J_2$ and $2J_3$. A small amount of paramagnetic impurities, $\rho = 0.016$, has also been found. The calculated curve matches very well the experimental data in the whole temperature range, as can be seen in Fig. 7. The observed $2J$ values can be correlated with the molecular structure by considering the magnetic exchange pathways between the copper(II) ions. $\text{Cu2} \cdots \text{Cu2}'$ are connected via a double μ_3 -OH bridge with a $\text{Cu2-O-Cu2}'$ bridging angle of 96.5° for which a ferromagnetic coupling of $\sim 127 \text{ cm}^{-1}$ is predicted [62,63]. The linkage between Cu1 and Cu2 takes place through μ_2 - N1:N2 -triazole and a μ_3 -OH bridge. The combination of these bridges leads to antiferromagnetic coupling that ranges from -50 to -236 cm^{-1} [64–67]. Finally the connection $\text{Cu1} \cdots \text{Cu2}$ is via a μ_3 -OH, a μ_2 -O(carboxylate) and a *syn-syn* carboxylate bridge. Due to the complementarity–anti-complementarity [68–70] phenomenon this bridging mode can lead to either ferro- or antiferromagnetic coupling with coupling constants that range from -260 to 120 cm^{-1} [71–75]. For the Cu1-O-Cu2 bridging angles found in **2** (88.6° and 97.6°) and the additional *syn-syn* carboxylate bridge moderate ferromagnetic coupling is predicted [76]. With the application of the model described in Scheme 2 the ferro or antiferromagnetic nature of the coupling constants has been satisfactorily obtained, however the values of the coupling constants are bigger than expected which might be due to a strong interdependence between the parameters in the mathematic equation of the magnetic susceptibility that the fitting procedure could not overcome.

2.7. Emission properties of **3**

The cadmium compound **3** shows a strong fluorescence emission at 421 nm upon excitation at 317 nm (Fig. 8). Benzene-1,3,5-tricarboxylic acid is not fluorescent and 1,2-bis(1,2,4-triazol-4-yl)ethane (btre) gives no fluorescence response at room temperature. The possible btre fluorescence through an intra-ligand charge transfer is apparently quenched by the thermal intra-ligand rotations around the C–C and C–N bonds. Fixation of the ligand in a coordination network stops the rotation and freezes a single conformation to enable the fluorescence. Thus, the cadmium mixed coordination polymer leads to a strong enhancement in fluorescence. An increase in fluorescence intensity is often seen in luminescence studies of zinc, cadmium, and silver coordination polymers [1,77].

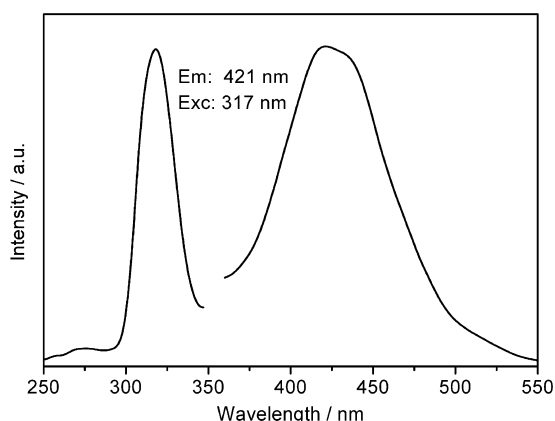


Fig. 8. Excitation and emission spectrum of compound **3**.

3. Conclusions

The ligand combination of 1,2-bis(1,2,4-triazol-4-yl)ethane (btre) and fully deprotonated benzene-1,3,5-tricarboxylate (btc^{3-}) with copper and cadmium cations leads to 3D metal-organic frameworks. Compound **2** is a framework constructed from a tetranuclear, chair-shaped Cu_4O_4 core. This arrangement of the metal ions is very frequent for Fe(III) [78] or Cr(III) and is usually called quasi-butterfly structure or defective double cubane structure [60,79]. We have calculated the Eigenvalues associated with the zero field spin Hamiltonian shown in Eq. (2) by solving the 16×16 matrix and we have obtained the numerical expression for the magnetic susceptibility. However, the magnetic coupling constants are somewhat bigger than that the expected ones. Cadmium coordination to the btre ligand in **3** turns on a luminescence response upon UV excitation (not seen in the free ligand).

4. Experimental

4.1. General methods and materials

Commercially available solvents, monoformylhydrazine, triethyl orthoformate, ethylenediamine, benzene-1,3,5-tricarboxylic acid (H_3btc), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, and $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$ were used without further purification. The ligand 1,2-bis(1,2,4-triazol-4-yl)ethane (btre) was prepared according to the method from Bayer [80]. Dried methanol is used for the preparation of the btre ligand. Elemental analyses were performed on a VarioEL from Elementaranalysensysteme GmbH. Infrared spectra were recorded in the range 400–4000 cm^{-1} on a Bruker Optik IFS 25 spectrophotometer using KBr pellets. Thermogravimetric analysis was carried out on a simultaneous thermoanalysis apparatus STA 409 from Netzsch under nitrogen with a heating rate of 10 $^\circ\text{C min}^{-1}$ in the range 25–600 $^\circ\text{C}$. The filled sample container was conditioned by first applying oil pump vacuum down to 1 bar for 5 min, then flushing with nitrogen. Powder X-ray diffraction patterns were measured at ambient temperature using a STOE STADI-P with Debye-Scherrer geometry, Mo $\text{K}\alpha$ radiation ($\lambda = 0.7093 \text{ \AA}$), a Ge(111) monochromator and the samples in glass capillaries on a rotating probe head. Simulated powder patterns were based on single-crystal data and calculated using the STOE WINXPOW software package [81]. Emission spectra were measured on a Perkin-Elmer LS-55, $\lambda_{\text{exc}} = 323 \text{ nm}$, split widths (em, ex) 5.0 nm, scan speed 2 nm s^{-1} , solid sample at room temperature. Magnetic susceptibility measurements on polycrystalline samples were carried out in the temperature range 1.9–300 K by means of a Quantum Design SQUID magnetometer operating at

10,000 Oe. Diamagnetic corrections of the constituent atoms were estimated from Pascal's constants. Experimental susceptibilities were also corrected for the temperature-independent paramagnetism [$60 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ per Cu(II)] and the magnetization of the sample holder.

4.2. X-ray crystallography

Suitable single crystals were carefully selected under a polarizing microscope. **Data Collection**: Bruker AXS Smart diffractometer for **1**, Bruker AXS with APEX2 CCD area-detector for **2** and **3**, Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), graphite monochromator, double-pass method ω -scan. **Data collection** with SMART [82] and APEX2 [83], respectively, cell refinement and data reduction with SAINT [82,83], experimental absorption correction with SADABS [84]. **Structure Analysis and Refinement**: The structure was solved by direct methods (SHELXS-97); [85] refinement was done by full-matrix least squares on F^2 using the SHELXL-97 program suite [85]. All non-hydrogen positions were refined with anisotropic temperature factors. Hydrogen atoms on the aromatic rings and the carbon atoms were placed at calculated positions with an appropriate riding

Table 2
Crystal data and structure refinement for **1–3**.

Compound	1	2	3
Empirical formula	$\text{C}_{24}\text{H}_{18}\text{CuN}_6\text{O}_{12}$	$\text{C}_{12}\text{H}_{10}\text{Cu}_2\text{N}_3\text{O}_8^e$	$\text{C}_{24}\text{H}_{16}\text{Cd}_3\text{N}_6\text{O}_{13}^f$
M (g mol^{-1})	645.99	451.31 ^e	933.63 ^f
Crystal size (mm)	$0.16 \times 0.09 \times 0.08$	$0.33 \times 0.15 \times 0.02$	$0.33 \times 0.12 \times 0.02$
2θ Range ($^\circ$)	3.6–51.5	4.2–51.1	4.5–68.4
Completeness to 2θ (%)	99.6	99.0	99.9 ^g
$h; k; l$ Range	± 8 ± 9 ± 14	± 11 $-6, +11$ $-16, +19$	± 13 ± 14 ± 15
Temperature (K)	203(2)	203(2)	296(2)
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a (\AA)	7.0888(8)	9.7355(8)	8.6582(2)
b (\AA)	8.0590(9)	9.2386(7)	9.1780(2)
c (\AA)	12.0399(13)	15.7272(13)	9.8954(3)
α ($^\circ$)	106.303(2)	90	101.167(2)
β ($^\circ$)	97.692(2)	97.802(2)	104.950(2)
γ ($^\circ$)	97.118(2)	90	114.4120(10)
V (\AA^3)	644.73(12)	1401.45(19)	650.25(3)
Z	1	4	1
D_{calc} (g cm^{-3})	1.664	2.139	2.379
$F(000)$	329	900	448
μ (mm^{-1})	0.927	3.089	2.517
Maximum/minimum transmission	0.9329/0.8636	0.9408/0.4288	0.9514/0.4906
Reflections collected (R_{int})	5111 (0.0525)	10218 (0.0462)	21099 (0.0451)
Independent reflections	2444	2597	5341
Observed reflections [$I > 2\sigma(I)$]	1574	2094	4331
Parameters refined	202	235	215
Maximum/minimum $\Delta\rho$ (e \AA^{-3}) ^a	0.567/−0.951	0.448/−0.498	0.833/−0.975
R_1/wR_2 [$I > 2\sigma(I)$] ^b	0.0540/0.1124	0.0357/0.0755	0.0310/0.0598
R_1/wR_2 (all reflect.) ^b	0.0954/0.1298	0.0502/0.0824	0.0446/0.0643
Goodness-of-fit on F^2 ^c	1.013	1.064	1.039
Weight. scheme $w; a/ b^d$	0.0562/0.0000	0.0344/1.19260	0.0210/0.7702

^a Largest difference peak and hole.

^b $R_1 = [\sum(|F_o| - |F_c|)] / \sum|F_o|$; $wR_2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$.

^c Goodness-of-fit = $[\sum[w(F_o^2 - F_c^2)^2] / (n - p)]^{1/2}$.

^d $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (\max(F_o^2 \text{ or } 0) + 2F_c^2) / 3$.

^e In the text the doubled formula of the asymmetric unit is used to have full ligand numbers.

^f H atoms on crystal water not located but included in formula and formula mass.

^g Completeness to $2\theta = 50^\circ$.

model (AFIX 43 for aromatic CH, AFIX 23 for CH₂) and an isotropic temperature factor of $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{CH}, \text{CH}_2)$. In **1** and **2** the hydrogen atoms of the carboxyl groups and the water of crystallization, respectively, were found and refined with $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{O})$ (see Table S1 in Supporting information). In **3** the hydrogen atoms of the half-occupied O atom of the crystal water near the inversion center were not found. Simulated X-ray powder diffractograms from the single-crystal data were matched with measured X-ray powder diffractograms for **2** and **3** to verify the representative nature of the single crystal with respect to the bulk material (Figs. S5 and S6 in Supporting information). Graphics were obtained with DIAMOND [86]. Crystal data and details on the structure refinement are given in Table 2.

4.3. Syntheses of catena-[bis(dihydrogen benzene-1,3,5-tricarboxylato-κO)-(μ-1,2-bis(1,2,4-triazol-4-yl)ethane-κ²N1:N1')copper(II)], $^1_{\infty}\{[\text{Cu}(\text{H}_2\text{btc})_2(\mu\text{-btre})]\}$, **1**

A mixture of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (185 mg, 0.50 mmol), H_3btc (105 mg, 0.50 mmol), triethylamine (210 μL, 1.50 mmol), btre (82 mg, 0.50 mmol) and water (10 mL) was stirred for 30 min at room temperature, transferred to a Teflon-lined stainless-steel autoclave and heated at 180 °C for 3 d. Then the autoclave was cooled to room temperature at a rate of 2.8 °C h⁻¹. A blue crystalline product, which was suitable for X-ray single crystal analysis was filtered off, washed with distilled water and dried in air (yield 85 mg, 75% based on Cu). Elemental Anal. Calc. for $\text{C}_{24}\text{H}_{20}\text{Cu}_4\text{N}_6\text{O}_{16}$ (902.62): C, 31.94; H, 2.22; N, 9.31. Found: C, 31.45; H, 2.33; N, 10.05%. IR (KBr) 3515 and 3424(w, ν(O–H)), 3136(w), 1640 and 1611(s, ν_{asym}CO₂), 1555(s, ν_{asym}CO₂), 1451(s, ν_{sym}CO₂), 1357(s, ν_{sym}CO₂), 1203(m, δ(OH...O)), 1163(w), 1079(s), 1053(s), 1022(w), 987(m), 936(w), 904(w, δ(OH...O)), 874(m), 839(w), 757(s), 722(s), 697(w), 642(s), 590(w), 562(w), 487(s), 457(s) cm⁻¹.

4.4. Syntheses of catena-[bis(μ₅-benzene-1,3,5-tricarboxylato-κ⁵O:O':O'':O''':O''')-bis(μ₃-hydroxo)-(μ₄-1,2-bis(1,2,4-triazol-4-yl)ethane-κ⁴N1:N2:N1':N2')-tetracopper(II) dihydrate, $^2_{\infty}\{[\text{Cu}_4(\mu_5\text{-btc})_2(\mu_3\text{-OH})_2(\mu_4\text{-btre})] \cdot 2\text{H}_2\text{O}\}$, **2**

A mixture of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (185 mg, 0.50 mmol), H_3btc (105 mg, 0.50 mmol), triethylamine (210 μL, 1.50 mmol), btre (82 mg, 0.50 mmol) and water (10 mL) was stirred for 30 min at room temperature, transferred to a Teflon-lined stainless-steel autoclave and heated at 180 °C for 3 d. Then the autoclave was cooled to room temperature at a rate of 2.8 °C h⁻¹. A blue crystalline product, which was suitable for X-ray single crystal analysis was filtered off, washed with distilled water and dried in air (yield 85 mg, 75% based on Cu). Elemental Anal. Calc. for $\text{C}_{24}\text{H}_{20}\text{Cu}_4\text{N}_6\text{O}_{16}$ (902.62): C, 31.94; H, 2.22; N, 9.31. Found: C, 31.45; H, 2.33; N, 10.05%. IR (KBr) 3515 and 3424(w, ν(O–H)), 3136(w), 1640 and 1611(s, ν_{asym}CO₂), 1555(s, ν_{asym}CO₂), 1451(s, ν_{sym}CO₂), 1357(s, ν_{sym}CO₂), 1203(m, δ(OH...O)), 1163(w), 1079(s), 1053(s), 1022(w), 987(m), 936(w), 904(w, δ(OH...O)), 874(m), 839(w), 757(s), 722(s), 697(w), 642(s), 590(w), 562(w), 487(s), 457(s) cm⁻¹.

4.5. Syntheses of catena-[bis(μ₆-benzene-1,3,5-tricarboxylato-κ⁶O:O':O'':O''':O''':O''':O''')-(μ₄-1,2-bis(1,2,4-triazol-4-yl)ethane-κ⁴N1:N2:N1':N2')-tricadmium(II) hydrate, $^3_{\infty}\{[\text{Cd}_3(\mu_6\text{-btc})_2(\mu_4\text{-btre})] \cdot \text{H}_2\text{O}\}$, **3**

A mixture of $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$ (256 mg, 1.00 mmol), H_3btc (210 mg, 1.00 mmol), triethylamine (420 μL, 3.00 mmol), btre (164 mg, 1.00 mmol) and water (10 mL) was stirred for 30 min at room temperature, transferred to a Teflon-lined stainless-steel autoclave and heated at 180 °C for 3 d. Then the autoclave was cooled to room temperature at a rate of 2.8 °C h⁻¹. A colorless crys-

talline product, which was suitable for X-ray single crystal analysis was filtered off, washed with distilled water and dried in air (yield 210 mg, 68% based on Cd). Elemental Anal. Calc. for $\text{C}_{24}\text{H}_{18}\text{Cd}_3\text{N}_6\text{O}_{14}$ (951.64): C, 30.29; H, 1.91; N, 8.83. Found: C, 29.29; H, 1.62; N, 8.88%. IR (KBr) 3423(w, ν(O–H)), 3127(w), 1610(s, ν_{asym}CO₂), 1559(s, ν_{asym}CO₂), 1430(s, ν_{sym}CO₂), 1371(s, ν_{sym}CO₂), 1202(w, δ(OH...O)), 1170(w), 1074(m), 1044(m), 1000(w), 918(m, δ(OH...O)), 859(s), 770(s), 723(s), 681(s), 644(s), 510(w), 440(w) cm⁻¹.

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Appendix A. Supplementary material

CCDC 707133, 707134, and 707135 contain the supplementary crystallographic data for **1**, **2**, and **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2008.11.003.

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