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Synthesis and Crystal Structure of two Cu(II)-benzene-1,2,4,5-tetracarboxylates with Three-Dimensional Open Frameworks

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Abstract. Two new three-dimensional frameworks with zeolite-like channels have been prepared in the presence of 1,6-diaminohexane. $\text{Cu}_{1.5}(\text{H}_3\text{N}-(\text{CH}_2)_6-\text{NH}_3)_{0.5}[\text{C}_6\text{H}_2(\text{COO})_4]\cdot 5\text{H}_2\text{O}$ (**1**) crystallizes in the triclinic space group *P*-1 with $a = 772.56(7)$, $b = 1110.36(7)$, $c = 1111.98(8)$ pm, $\alpha = 98.720(7)^\circ$, $\beta = 108.246(9)^\circ$ and $\gamma = 95.559(7)^\circ$. $\text{Cu}_2(\text{H}_3\text{N}-(\text{CH}_2)_6-\text{NH}_3)_{0.5}(\text{OH})[\text{C}_6\text{H}_2(\text{COO})_4]\cdot 3\text{H}_2\text{O}$ (**2**) crystallizes in the monoclinic space group *P*2/*c* with $a = 1159.34(11)$, $b = 1059.44(7)$, $c = 1582.2(2)$ pm and $\beta = 106.130(11)^\circ$.

The Cu^{2+} coordination polyhedra are connected by $[\text{C}_6\text{H}_2(\text{COO})_4]^{4-}$ anions to yield three-dimensional frameworks with wide centrosymmetric channel-like voids. Complex **1** reveals voids extending along [100] with diagonals of 900 pm and 300 pm, whereas in complex **2** the diagonal of the nearly rectangular crosssection of the channels extending parallel to [001] is 900 pm. The negative excess charges of the frameworks are compensated by $[\text{H}_3\text{N}-(\text{CH}_2)_6-\text{NH}_3]^{2+}$ -cations, which occupy the voids along with water molecules. The $[\text{H}_3\text{N}-(\text{CH}_2)_6-\text{NH}_3]^{2+}$ -cations are not connected to Cu^{2+} and have served as templates.

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Introduction

With multi-dentate complexing agents like the anions of benzenecarboxylic acids it is possible to form coordination polymers with various structural features [1–10]. The carboxylate groups of benzenecarboxylic acids anions are able to coordinate metal ions in various modes, resulting in a plethora of interesting structures. Early reports have shown that the connection between the anions of benzene-1,2,4,5-carboxylic acid (pyromellitic acid) and metal cations leads to coordination polymers with chain- and layer-like structures as well as to three-dimensional frameworks (so-called MOF's) [11–14]. The structures of coordination polymers can be varied using rational design synthesis e.g. N-donor ligands as spacer and organic amines as template molecules, respectively [15–23]. In particular, three-dimensional frameworks are available in the presence of organic amines acting as template molecules [24–28]. Previous work on the reaction between Cu^{2+} and benzene-1,2,4,5-carboxylic acid in the presence of templating agents resulted in various three-dimensional frameworks with

channel-like voids resembling zeolite structures [29–35]. Additionally, Cu^{2+} -benzenecarboxylato complexes can possess interesting magnetic properties [21,30,31,33,35] and they can act as catalysts for e.g. peroxidative oxidation processes, for hydroxylation reactions, and for the reduction of nitrite [32,36,37].

Here we report on two new three-dimensional coordination polymers with wide channels as a result of the connection between Cu^{2+} -cations and benzene-1,2,4,5-tetracarboxylate anions in the presence of 1,6-diaminohexane as template at two different temperatures of synthesis.

Results and Discussion

$\text{Cu}_{1.5}(\text{H}_3\text{N}-(\text{CH}_2)_6-\text{NH}_3)_{0.5}[\text{C}_6\text{H}_2(\text{COO})_4]\cdot 5\text{H}_2\text{O}$ (**1**). There are two crystallographically independent Cu^{2+} -ions. Cu(1) occupies the general position and Cu(2) a crystallographic inversion centre of space group *P*-1 (Wyckoff-position 1a). Cu(1) is coordinated by three 1,2,4,5-benzenetetracarboxylate oxygen atoms (O(2), O(4), O(5), O(8)) and one water molecule (O(w1)) forming a distorted square pyramid. Cu(2) is octahedrally coordinated by four oxygen atoms (2x O(1), 2x O(6)) stemming from the 1,2,4,5-benzenetetracarboxylate-anion in the equatorial plane of the coordination octahedron and two water molecules (2x O(w2)) in the apical positions (Fig. 1). The carboxylate groups of the $[\text{C}_6\text{H}_2(\text{COO})_4]^{4-}$ anions coordinate the Cu^{2+} -cations in a monodentate manner. The Cu–O distances in the Cu(1) coordination polyhedron range from 192.6(2) to 240.0(2) pm, with the Cu(1)–OH₂ contact as the

shortest bond. The Cu(2) polyhedron has Cu–O bond lengths between 194.4(2) and 243.1(2) pm with the Cu(2)–OH₂ contact as the longest bond and in contrast to Cu(1) (Tab. 1). The bond order (Cu(1) 2.04; Cu(2) 1.94) calculated by the method of Trömel [38,39] is close to the expected values.

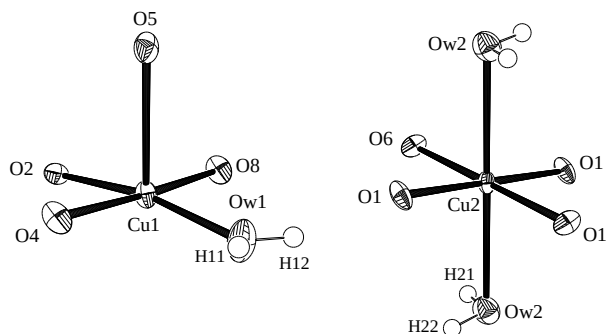


Figure 1. The coordination spheres of Cu(1) and Cu(2) in **1** (50 % probability ellipsoids, arbitrary radii for hydrogen atoms).

Table 1. The Coordination of Cu²⁺ in Cu_{1.5}(H₃N-(CH₂)₆-NH₃)_{0.5}[C₆H₂(COO)₄]·5H₂O (**1**)

bond lengths (pm)			
Cu(1)–O(w1)	192.6(2)	Cu(2)–O(6)	194.4(2) 2x
Cu(1)–O(8)	196.0(2)	Cu(2)–O(1)	202.0(2) 2x
Cu(1)–O(4)	193.7(2)	Cu(2)–O(w2)	243.1(2) 2x
Cu(1)–O(2)	198.3(2)		
Cu(1)–O(5)	240.0(2)		
bond angles (°)			
O(w1)–Cu(1)–O(4)	91.97(8)	O(6) [#] –Cu(2)–O(6)	180
O(w1)–Cu(1)–O(8)	91.45(8)	O(6) [#] –Cu(2)–O(1)	90.82(7)
O(4)–Cu(1)–O(8)	176.42(7)	O(6)–Cu(2)–O(1)	89.18(7)
O(w1)–Cu(1)–O(2)	168.94(8)	O(1)–Cu(2)–O(1) [#]	180
O(4)–Cu(1)–O(2)	87.66(7)	O(6) [#] –Cu(2)–O(w2)	82.52(7)
O(8)–Cu(1)–O(2)	89.18(7)	O(6)–Cu(2)–O(w2)	97.49(7)
O(w1)–Cu(1)–O(5)	96.28(8)	O(1)–Cu(2)–O(w2)	86.03(7)
O(4)–Cu(1)–O(5)	83.49(7)	O(1)–Cu(2)–O(w2) [#]	93.97(7)
O(8)–Cu(1)–O(5)	95.12(7)	O(w2)–Cu(2)–O(w2) [#]	180
O(2)–Cu(1)–O(5)	94.66(6)		

#: -x;-y;-z

The two crystallographically independent [C₆H₂(COO)₄]⁴⁻ anions (I, II) are located on an inversion centre (Fig. 2). Anion I is almost ideally planar with respect to the carbon atoms. The largest deviation from a plane fitted to the carbon skeleton is merely 1.6 pm at C(5). The carboxylate groups are inclined to the C₆ ring by 35.5° (C(7), O(1), O(2)) and 64.1° (C(8), O(3), O(4)). Anion II is planar as well in good approximation. C(9) is 28.4 pm out of the plane fitted to the carbon skeleton. The angle of torsion with respect to the C₆ ring is 20.6° (C(12), O(5), O(6)) and 41.8° (C(13), O(7), O(8)), respectively. The C–O bond lengths of the anions range from 122.7(3) to 128.9(3). The oxygen atoms bound to Cu²⁺ form significant longer C–O bonds

than the others (O(3), O(7)) (Tab. 2). As shown in Fig. 3 the [C₆H₂(COO)₄]⁴⁻ anion I is arranged parallel to the (010) plane, whereas anion II is parallel to the (201) plane.

Table 2. Selected Bond Lengths (pm) and Angles (°) of the Benzene-1,2,4,5-tetracarboxylate-anions and the Hexane-1,6-diammonium-cation in **1**

Anion I			
C(4)–C(6)	139.4(3)	C(7)–O(1)	126.3(3)
C(4)–C(5)	140.3(3)	C(7)–O(2)	126.4(3)
C(5)–C(6)	139.4(3)	C(8)–O(3)	123.8(3)
C(4)–C(7)	151.2(3)	C(8)–O(4)	127.0(3)
C(5)–C(8)	151.9(3)		
C(6)–C(4)–C(5)	119.5(2)	O(2)–C(7)–O(1)	123.0(2)
C(6)–C(4)–C(7)	117.4(2)	O(1)–C(7)–C(4)	116.3(2)
C(6) ^{#3} –C(5)–C(4)	118.5(2)	O(2)–C(7)–C(4)	120.7(2)
C(5)–C(4)–C(7)	123.1(2)	O(3)–C(8)–O(4)	123.5(2)
C(6) ^{#3} –C(5)–C(8)	117.1(2)	O(3)–C(8)–C(5)	117.2(2)
C(4)–C(5)–C(8)	124.3(2)	O(4)–C(8)–C(5)	119.2(2)
C(4)–C(6)–C(5) ^{#3}	121.9(2)		
Anion II			
C(9)–C(10)	140.4(3)	C(12)–O(5)	125.1(3)
C(9)–C(11)	138.6(3)	C(12)–O(6)	126.7(3)
C(10)–C(11)	138.6(3)	C(13)–O(7)	122.7(3)
C(10)–C(13)	150.7(3)	C(13)–O(8)	128.9(3)
C(9)–C(12)	151.2(3)		
C(11) ^{#4} –C(9)–C(10) ^{#5}	119.0(2)	O(5)–C(12)–O(6)	126.0(2)
C(10) ^{#5} –C(9)–C(12)	122.2(2)	O(5)–C(12)–C(9)	119.2(2)
C(11) ^{#4} –C(9)–C(12)	118.7(2)	O(6)–C(12)–C(9)	114.7(2)
C(11)–C(10)–C(9) ^{#6}	119.2(2)	O(7)–C(13)–O(8)	123.5(2)
C(11)–C(10)–C(13)	117.9(2)	O(7)–C(13)–C(10)	120.2(2)
C(9) ^{#6} –C(10)–C(13)	122.7(2)	O(8)–C(13)–C(10)	116.1(2)
C(9) ^{#4} –C(11)–C(10)	121.8(2)		
Hexane-1,6-diammonium-cation			
N–C(1)	149.0(4)	C(2)–C(3)	152.0(4)
C(1)–C(2)	150.5(4)	C(3)–C(3) ^{#2}	151.7(6)
N–C(1)–C(2)	112.2(2)	C(3) ^{#1} –C(3)–C(2)	113.0(3)
C(1)–C(2)–C(3)	112.2(3)		

#1: -x;-y;-z, #2: -x;-y-1;-z-1, #3: -x;-y;-z-1, #4: -x+1;-y+1;-z, #5: x+1;y;z, #6: x-1;y;z

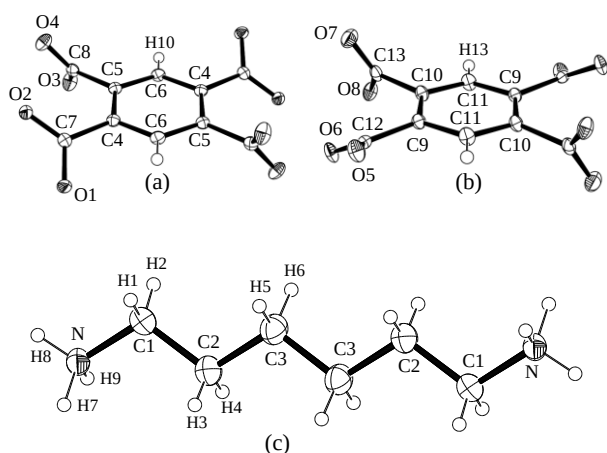


Figure 2. The [C₆H₂(COO)₄]⁴⁻ anions I (a) and II (b) as well as the hexane-1,6-diammonium-cation (c) in **1** (50 % probability ellipsoids, arbitrary radii for hydrogen atoms).

The connection between the Cu(2)-cations and the [C₆H₂(COO)₄]⁴⁻ anions results in a three-dimensional zeolite-like framework with channel-like voids extending along [100] (Fig. 3 and 4), whereas the coordination between the Cu(1)-cations and the [C₆H₂(COO)₄]⁴⁻ anions only leads to a stabilization of the structure by lowering the negative charge of the framework. The oxygen atoms of the carboxylate groups coordinate only in a monodentate manner. The diagonals as the largest and narrowest openings of the channel-like voids are approximately 900 pm and 300 pm, respectively, with the *van-der-Waals* radii [40] of the framework atoms taken into account. The voids are occupied by water molecules not bound to Cu²⁺ and [(CH₂)₆(NH₃)₂]²⁺-cations, which compensate for the negative excess charge of the {[(Cu(H₂O))₂Cu(H₂O)₂][C₆H₂(COO)₄]₂]_n²ⁿ⁻ framework. The [(CH₂)₆(NH₃)₂]²⁺-cations adopt an antiperiplanar conformation and are located on a crystallographic inversion centre (Fig. 2). The C–C bond lengths range from 150.4(4) to 152.0(4) pm and the C(1)–N bond is slightly shorter (149.0(4) pm).

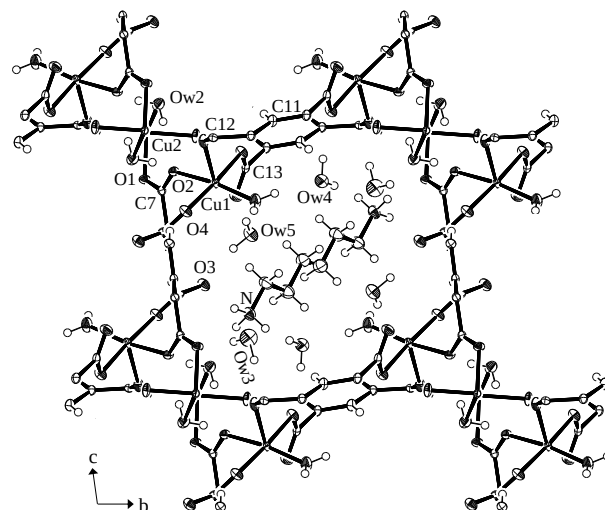


Figure 3. The crystal structure of **1** viewed from [100] showing centrosymmetric channel-like voids (50 % probability ellipsoids, arbitrary radii for hydrogen atoms).

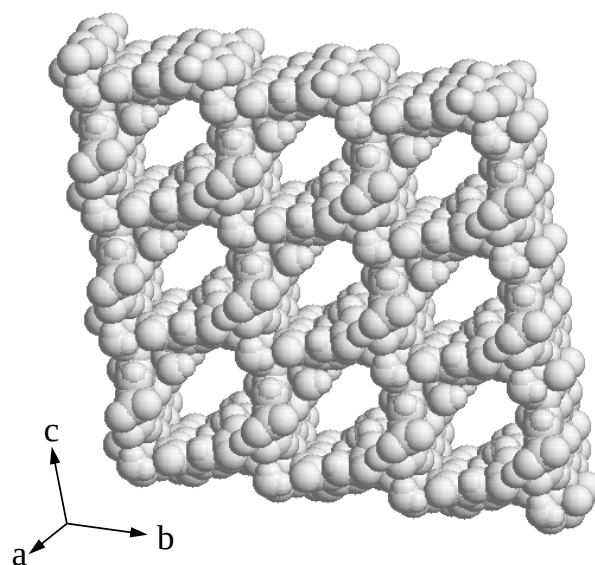


Figure 4. Space filling model of **1** (hexane-1,6-diammonium-cations and guest water molecules are omitted).

The water molecules (O(w3), O(w4) and O(w5)) which are not connected to Cu²⁺ serve to stabilize the crystal structure by hydrogen bonds. The NH₃⁺ groups of the 1,6-diammoniumhexane-cations act as proton donors for O(w4) and the carboxylate oxygen atoms O(1) and O(3). With exception of O(6) all carboxylate oxygen atoms are involved in hydrogen bonds as proton acceptors. The O...O distances range from 258.9 to 302.2 pm indicating rather strong hydrogen bonding besides hydrogen bonds of smaller strength [41,42] (Tab. 3).

Table 3. Hydrogen bonds in **1**

N...O Distance (pm)			
N-H(7)...O(1)	287.7	N-H(9)...O(w4)	295.5
N-H(8)...O(3)	283.7		
O...O Distance (pm)			
O(w2)-H(21)...O(4)	302.2	O(w5)-H(52)...O(3)	276.8
O(w2)-H(21)...O(5)	287.8	O(w1)-H(11)...O(w5)	258.9
O(w2)-H(22)...O(2)	276.8	O(w1)-H(12)...O(w4)	274.4
O(w3)-H(31)...O(5)	286.8	O(w3)-H(32)...O(w2)	289.1
O(w4)-H(42)...O(8)	278.9	O(w4)-H(41)...O(w3)	275.5
O(w5)-H(51)...O(7)	276.1		

1 loses water of crystallization upon storage in a desiccator over sulphuric acid yielding a trihydrate (molecular weight 458.62). The elemental analysis yields C: 34.44%, H: 3.72%, and N: 2.94%, which agree very well with the expected values for a trihydrate (C: 34.05%, H: 3.74%, N: 3.05%). The single crystals decayed to small pieces which could be rehydrated to the pentahydrate when stored in humid atmosphere. The rehydrated pentahydrate showed the same X-Ray powder diffraction pattern as the starting material (Fig. 5). The elemental analysis confirmed also the formation of a pentahydrate (molecular weight 494.62; exp./calc.: C: 31.45/31.57 %, H: 4.18/4.28 %, N: 2.66/2.83%).

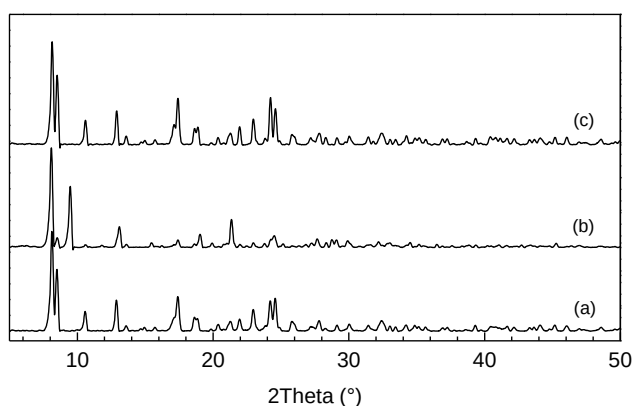


Figure 5: X-ray powder diffraction patterns of **1** (a), dehydrated sample (trihydrate) (b), and rehydrated sample (pentahydrate) (c).

Si et al. [43] reported on three-dimensional framework in a copper benzene-1,2,4,5-tetracarboxylate accommodating piperidine molecules. However, this compound features chains made up from Cu^{2+} and $[\text{C}_6\text{H}_2(\text{COOH})_2(\text{COO})_2]^{2-}$ which are cross-linked by solely hydrogen bonds to H_2O and uncoordinated benzene-1,2,4,5-tetracarboxylic acid.

$\text{Cu}_2(\text{H}_3\text{N}-(\text{CH}_2)_6-\text{NH}_3)_{0.5}(\text{OH})[\text{C}_6\text{H}_2(\text{COO})_4] \cdot 3\text{H}_2\text{O}$, (**2**). There are two crystallographically independent Cu^{2+} -ions occupying general positions of space group P2/c. Cu(1) is coordinated in a distorted square pyramidal fashion by three

carboxylate oxygen atoms (O(4), O(6), O(8)) and twice by O(9) stemming from hydroxo groups. Two coordination polyhedra of Cu(1) correlated by a crystallographic inversion center are linked by a common edge (2x O(9)) yielding a short Cu(1)-Cu(1) contact of 291.76(8) pm. Recently, Mihalcea et al. [44] reported on similar bridging of metal centres by hydroxo groups in uranyl benzene-1,2,4,5-tetracarboxylate complexes. The Cu(2) cation is surrounded in a distorted trigonal bipyramidal manner by four carboxylate oxygen atoms (O(1), O(3), O(5), O(7)) and one hydroxo oxygen atom (O(9), Tab. 4). The bond angles O(5)-Cu(2)-O(3) and O(7)-Cu(2)-O(5) deviate from 120° considerably. O(9) is a common corner of the coordination polyhedra of Cu(1) and Cu(2) (Fig. 6). Employing the method of Trömel [38,39] the bond order is calculated to 2.20 (Cu(1)) and 1.94 (Cu(2)), respectively. Chiang et al. [45] reported on a similar hydroxo-bridged tetranuclear unit in a cobalt benzene-1,2,4,5-tetracarboxylate.

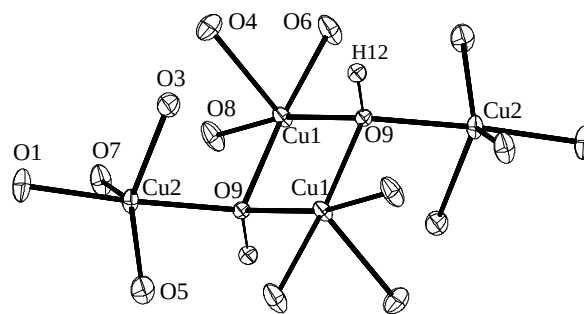


Figure 6. The coordination environments of Cu^{2+} in **2** (Ellipsoids are given at 50% probability).

There are also two crystallographically independent $[\text{C}_6\text{H}_2(\text{COO})_4]^{4-}$ anions. The bond lengths and bond angles are comparable to those of the anions in compound **1**. The centrosymmetric anion I is almost planar with respect to the carbon skeleton. The largest deviation from a plane fitted to the carbon atoms is 5.4 pm (C6). The carboxylate groups are twisted against the C_6 -ring by 25.8° (C(7), O(1), O(2)) and 66.5° (C(8), O(3), O(4)), respectively. The C–O bond lengths range from 123.6(5) to 127.1(5) pm. The shortest C–O bond is formed by O(2) which is not connected to Cu^{2+} . The carbon skeleton of anion II which has C_2 symmetry is planar with a largest out of plane deviation of 3.3 pm for C(11). All oxygen atoms from this anion are involved in the Cu^{2+} coordination. The carboxylate groups show torsions angles of 49.0° (C(12), O(5), O(6)) and 46.5° (C(13), O(7), O(8)) with respect to the C_6 -ring. The variation of the C–O bond lengths between 124.2 (7) and 127.1(4) pm is related with the corresponding Cu–O bond lengths.

The monodentate coordination between the benzene-1,2,4,5-tetracarboxylate anions and the Cu^{2+} -cations builds up a three-dimensional framework with large channel-like

voids along [001] (Fig. 7 and 8). The square-like crosssection of the channels has a diagonal of 900 pm with the *van-der-Waals* radii [40] of the framework atoms taken into account. The channels accommodate water molecules not bound to Cu^{2+} and hexane-1,6-diammonium-cations compensating for the negative excess charge of the framework. Analogous to **1** the centrosymmetric hexane-1,6-diammonium-cations are in antiperiplanar conformation. The terminal nitrogen atoms, however, show a small deviation (7.6 pm) from a plane fitted to the $[\text{N}-\text{C}_6-\text{N}]^{2+}$ chain. The $\text{C}(1)-\text{N}$ bond length is 148.3(8) and the C–C bonds range from 149.7(11) pm to 153.5 (11) pm.

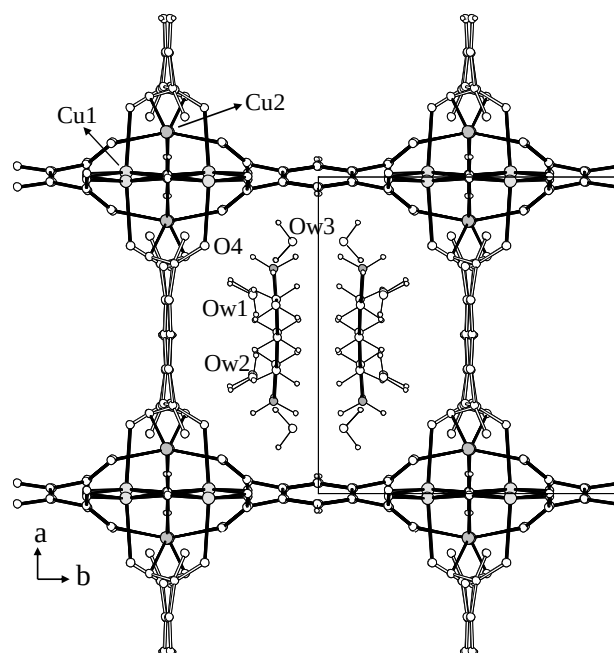


Figure 7. Crystal structure of **2** viewed along [001] showing the square-like channels (50 % probability ellipsoids, arbitrary radii for hydrogen atoms).

Table 4. The Coordination of Cu^{2+} in $\text{Cu}_2(\text{H}_3\text{N}-(\text{CH}_2)_6-\text{NH}_3)_{0.5}(\text{OH})[\text{C}_6\text{H}_2(\text{COO})_4] \cdot 3\text{H}_2\text{O} (**2**)$

bond lengths (pm)			
Cu(1)–O(6)	192.3(3)	Cu(2)–O(9)	191.7(2)
Cu(1)–O(9)	194.5(2)	Cu(2)–O(7)	203.4(3)
Cu(1)–O(4)	227.5(2)	Cu(2)–O(3)	223.0(3)
Cu(1)–O(8)	192.5(3)	Cu(2)–O(1)	192.9(2)
		Cu(2)–O(5)	206.1(3)
Cu(1)–Cu(1) [#]	291.76(8)		
bond angles (°)			
O(6)–Cu(1)–O(8)	88.53(11)	O(9)–Cu(2)–O(7)	89.56(10)
O(8)–Cu(1)–O(9) [#]	167.86(11)	O(9)–Cu(2)–O(5)	91.60(10)
O(8)–Cu(1)–O(9)	92.45(10)	O(7)–Cu(2)–O(5)	143.29(11)
O(6)–Cu(1)–O(4)	89.51(11)	O(1)–Cu(2)–O(3)	87.82(11)
O(9)–Cu(1)–O(4)	89.63(10)	O(5)–Cu(2)–O(3)	93.30(11)
O(6)–Cu(1)–O(9) [#]	94.96(10)	O(9)–Cu(2)–O(1)	175.12(11)
O(6)–Cu(1)–O(9)	175.43(11)	O(1)–Cu(2)–O(7)	93.60(11)
O(9) [#] –Cu(1)–O(9)	83.18(10)	O(1)–Cu(2)–O(5)	88.08(11)
O(8)–Cu(1)–O(4)	102.04(11)	O(9)–Cu(2)–O(3)	87.34(10)
O(9)–Cu(1)–O(4) [#]	94.64(10)	O(7)–Cu(2)–O(3)	123.40(11)
Cu(2)–O(9)–Cu(1)	113.45(12)	Cu(1) [#] –O(9)–Cu(1)	96.82(10)

[#]: -x; -y+1; -z

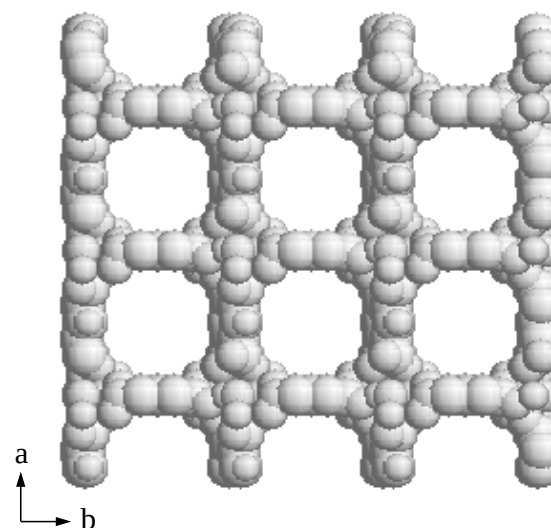


Figure 8. Space filling model of **2** (hexane-1,6-diammonium-cations and guest water molecules are omitted).

Table 5. Hydrogen bonds in **2**

N...O Distances (pm)			
N–H(1)···O(w2)	292.1	N–H(2)···O(4)	278.6
N–H(3)···O(w3)	278.6		
O...O Distances (pm)			

O(9)–H(12)···O(2)	256.6	O(w1)–H(13)···O(w2)	289.4
O(w1)–H(14)···O(3)	274.1	O(w2)–H(16)···O(w1)	289.3
O(w2)–H(15)···O(1)	302.8	O(w3)–H(18)···O(w1)	283.8
O(w3)–H(17)···O(8)	286.2		

Hydrogen bonds between carboxylate oxygen atoms and water molecules contribute to the stabilization of the framework. Except of O(5), O(6) and O(7) the carboxylate oxygen atoms are involved in hydrogen bonds. The oxygen atom O(2) which is not connected to Cu²⁺ acts as proton acceptor in a very strong hydrogen bond (256.6 pm) to the hydroxo group O(9)–H(12), which coordinated to three Cu²⁺. O(w1) and O(w2) as well as O(w1) and O(w3) are linked together by hydrogen bonds. The hexane-1,6-diammonium-cation acts as proton donator for O(w2), O(w3) and the carboxylate oxygen atom O(4) (Tab. 5).

Conclusions

In summary, we reported on the synthesis and crystal structures of two Cu(II)-benzene-1,2,4,5-tetracarboxylates in the presence of 1,6-diaminohexane as template agent. The connection between the Cu²⁺-ions and the benzene-1,2,4,5-tetracarboxylate-anions leads to three-dimensional frameworks with negative excess charge and channel-like voids. The voids accommodate hexane-1,6-diammonium-cations and water molecules, which are not connected to Cu²⁺.

Experimental Section

Single crystals of Cu_{1.5}(H₃N-(CH₂)₆-NH₃)_{0.5}[C₆H₂(COO)₄]·5H₂O (**1**) and Cu₂(H₃N-(CH₂)₆-NH₃)_{0.5}(OH)[C₆H₂(COO)₄]·3H₂O (**2**) were synthesized in the presence of 1,6-diaminohexane. An aqueous solution of 5ml 0.1M Cu(NO₃)₂ was added to a solution of 5ml 0.2M 1,6-diaminohexane. A precipitate, which appeared intermediately, was dissolved by addition of a small amount of 2M HNO₃. Then a solution of 5ml 0.05M sodium benzene-1,2,4,5-tetracarboxylate and 0.2 g urea were added. For **1**, the resulting solution was heated at 55°C for 3 days in a drying oven yielding light-blue crystals. To obtain compound **2**, the solution was heated at 80°C for 48h resulting in turquoise crystals. In contrast to the synthesis at 55°C, during the reaction at 80°C we observed a significant increase of the pH-value due the decomposition of urea. Results of elemental analyses: **1**: (molecular weight 494.62) C 31.39 (calc. 31.57); H 4.28 (4.50); N 2.83 (2.78)%. **2**: (molecular weight 507.36) C 30.03 (30.78); H 3.65 (3.58); N 2.72 (2.76)%. IR-ATR (cm⁻¹): **1**: 3448(m), 3295(m), 3099(m), 3036(w), 2946(w), 1673(w), 1598(s), 1599(s), 1489(s), 1367(s), 1325(s), 1277((m), 1133(s), 1049(w), 943(m), 919(m), 874(m), 831(m), 812(m), 765(m), 669(s), 617(m). **2**: 3445(m), 3238(w), 3182(m), 3058(w), 2960(w), 2873(w), 1679(w), 1630(w), 1574(s), 1492(s), 1426(m), 1376(s), 1323(s), 1289(m), 1141(m), 1108(m), 1040(m), 932(m), 867(m), 816(s), 763(m), 667(m), 611(s).

The TGA/DTA studies (Fig. 9) were carried out in air from room temperature to 1000°C at a heating rate of 10 K/min using a Netzsch STA-429 device. With **1**, a sharp endothermic process

between 161°C and 180 °C caused a weight loss of 17.8%, corresponding to the loss of the water molecules. The dehydrated compound was stable up to 250 °C. Several exothermic decomposition processes up to 1000 °C caused a total weight loss of 79.3%. With **2**, an endothermic weight loss between 100 and 230°C (10.2%) corresponds to the loss of all water molecules followed by a further weight loss of 3.4% up to 260 °C, which can be associated to the removal of water stemming from dehydroxylation of OH-groups. The following decomposition processes up to 1000 °C of the dehydrated sample caused a total weight loss of 75.1%. The residue in both cases contained Cu₂O and CuO which were identified by X-ray powder diffraction.

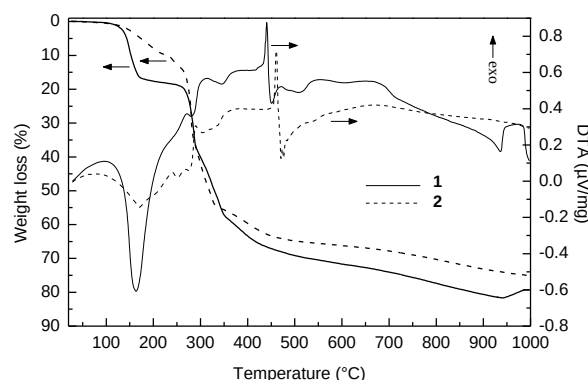


Fig. 9: Thermal analysis of compound **1** and **2**.

ATR Fourier transformed infrared (IR-ATR) measurements were carried out at room temperature using a Bio-rad FTS 25. X-Ray powder diffraction patterns were collected at room temperature on a Siemens D5000 (CuKα, germanium monochromator). X-ray single crystal structure determination was performed on a Siemens P4 four-circle diffractometer (MoKα, graphite monochromator) in a theta range up to 25.00°. Numerical absorption corrections have been applied. Extinction effects have been compensated for by introduction of an extinction parameter. The phase problem was solved by direct methods. Full matrix least squares refinement employing |F|² made use of the SHELXTL program suite [46]. Difference Fourier maps revealed the positions of all hydrogen atoms. They were allowed to refine individually with different common isotropic displacement parameters. Crystallographic data are given in Table 6.

Further details concerning the crystal structure analyses have been deposited with Cambridge Crystallographic Data Centre, The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK, Fax +(1223)336-033, e-mail data_request@ccdc.cam.ac.uk, www.ccdc.cam.ac.uk/data_request.cif under CCDC 941917 and CCDC 941918.

Table 6. Crystallographic Data

	1	2
Empirical formula	C ₁₃ H ₂₁ NCu _{1.5} O ₁₃	C ₁₃ H ₁₈ NCu ₂ O ₁₂
Crystal system	triclinic	monoclinic
Space group	P-1 (no.2)	P2/c (no.13)
Lattice constants	a = 772.56(7) pm b = 1110.36(7) pm	a = 1159.34(11) pm b = 1059.44(7) pm

	c = 1111.98(8) pm	c = 1582.2(2) pm
	$\alpha = 98.720(7)^\circ$	$\beta = 106.130(11)^\circ$
	$\beta = 108.246(9)^\circ$	
	$\gamma = 95.559(7)^\circ$	
Cell volume	0.88480(12) nm ³	1.8669(3) nm ³
Formulas in unit cell	2	4
Formula weight	494.62 g/mol	507.36 g/mol
Density (calc.)	1.857 g/cm ³	1.805 g/cm ³
Wavelength	71.073 pm	
Absorption coefficient	1.893 mm ⁻¹	2.342 mm ⁻¹
numerical	min./max.	min./max.
Absorption correction	transmittance	transmittance
	0.644/0.895	0.747/0.778
Temperature	293(2) K	
Crystal size (mm)	0.06 x 0.26 x 0.48	0.14 x 0.14 x 0.46
F (000)	507	1028
Θ -range	2.44° – 25.00°	2.34° – 24.99°
Limiting indices	h -1/+9 k -12/+12	h -1/+13 k -1/+12
	l -13/+12	l -18/+18
Reflections collected	3848	4266
Independent reflections	3104 ($R_{\text{int}} = 0.0196$)	3297 ($R_{\text{int}} = 0.0194$)
Structure solution	Direct methods	
Structure refinement	Full-matrix least-squares on $ F ^2$	
Refined parameters	327	313
Extinction parameter	0.0061(4)	0.0101(3)
Final mean shift/esd	0.006	0.006
Goodness-of-fit on $ F ^2$	1.213	1.407
Residuals (all data)	$R_1 = 0.0308$, $wR_2 = 0.0581$	$R_1 = 0.0420$, $wR_2 = 0.0720$
Max. features in last difference Fourier synthesis	322 and -351e·nm ⁻³	995 and -489e·nm ⁻³

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