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Synthesis, Crystal Structure, Hydrogen Bonding and Thermal Behaviour of a Three-Dimensional Cu(II)-benzene-1,2,4,5-tetracarboxylate Templated by 1,9-Diaminononane

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Dedicated to Professor Dr. Volker Woest on the Occasion of His 60th Birthday.

Keywords: Benzene-1,2,4,5-tetracarboxylate; Metal-organic-framework, Crystal structure; Template synthesis; Diaminononane

Abstract. Triclinic single crystals of $\text{Cu}_4(\text{H}_3\text{N}-(\text{CH}_2)_9-\text{NH}_3)(\text{OH})_2[\text{C}_6\text{H}_2(\text{COO})_4]_2 \cdot 5\text{H}_2\text{O}$ have been prepared in aqueous solution at 80 °C in the presence of 1,9-diaminononane. Space group *P*-1 (no. 2) with $a = 1057.5(2)$, $b = 1166.0(2)$, $c = 1576.7(2)$ pm, $\alpha = 106.080(10)^\circ$, $\beta = 90.73(2)^\circ$ and $\gamma = 94.050(10)^\circ$. The four crystallographic independent Cu^{2+} ions are surrounded by five oxygen atoms each with Cu–O distances between 191.4(3) and 231.7(4) pm. The connection between the Cu^{2+} coordination polyhedra and the $[\text{C}_6\text{H}_2(\text{COO})_4]^{4-}$ anions leads to a three-dimensional framework with negative excess charge and wide centrosymmetric channel-like voids.

These voids extend parallel to [001] with the diagonal of the nearly rectangular cross-section of approximately 900 pm. The channels of the framework accommodate $[\text{H}_3\text{N}-(\text{CH}_2)_9-\text{NH}_3]^{2+}$ -cations and water molecules, which are not connected to Cu^{2+} . The nonane-1,9-diammonium-cations adopt a partial *gauche* conformation. Thermoanalytical measurements in air show a loss of water of crystallization starting at 90 °C and finishing at approx. 170 °C. The dehydrated compound is stable up to 260 °C followed by an exothermic decomposition yielding copper oxide.

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Introduction

Multi-dentate complexing agents are very well suited to form coordination polymers with various structural features, if they are linked to suitable metal cations [1–12]. The carboxylate groups of benzenecarboxylic acids anions are able to coordinate metal ions in flexible modes. In particular the coordination 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) [13–17]. The structures of such coordination polymers can be varied using rational design synthesis e.g. N-donor ligands as spacers and organic amines as template molecules, respectively [18–28]. In the presence of organic amines as template molecules three-dimensional

frameworks are available [29–34]. 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 [35–41]. Moreover, Cu^{2+} -benzenecarboxylato complexes show interesting magnetic properties [26,36,37,39,41,42] and they are suitable as catalysts for e.g. peroxidative oxidation processes, for hydroxylation and isomerisation reactions, as well as for the reduction of nitrite [38,43–46].

We are interested in the influence of diamines with various chain-lengths as template agents on the structures of Cu^{2+} -benzene-1,2,4,5-tetracarboxylato complexes. In previous work we used 1,4-diaminobutane [41] and 1,6-diaminohexane [47] as templates. Here we report on the formation of a copper benzene-1,2,4,5-tetracarboxylate in the presence of 1,9-diaminononane.

Results and Discussion

In $\text{Cu}_4(\text{H}_3\text{N}-(\text{CH}_2)_9-\text{NH}_3)(\text{OH})_2[\text{C}_6\text{H}_2(\text{COO})_4]_2 \cdot 5\text{H}_2\text{O}$ there are four crystallographically independent Cu^{2+} -ions occupying general positions of space group *P*-1. Cu(1) is coordinated in a distorted square pyramidal fashion by three carboxylate oxygen atoms (O(3), O(6), O(13)) and twice by

O(18) stemming from hydroxo groups. Two coordination polyhedra of Cu(1) correlated by a crystallographic inversion center are linked by a common edge (2x O(18)) yielding a short Cu(1)–Cu(1) contact of 292.27(12) pm. Mihalcea et al. [48] reported on similar bridging of metal centres by hydroxo groups in uranyl benzene-1,2,4,5-tetracarboxylate complexes. The Cu(3) cation is surrounded in a distorted trigonal bipyramidal manner by four carboxylate oxygen atoms (O(4), O(5), O(9), O(14)) and one hydroxo oxygen atom (O(18), Tab. 1). O(18) is a common corner of the coordination polyhedra of Cu(1) and Cu(3) (Fig. 1). The Cu(2) and Cu(4) cations are surrounded in a similar manner and the polyhedra are bridged by common hydroxo groups (2x O(17)) resulting in a Cu(2)–Cu(2) contact of 294.89(13) pm. Employing the method of Trömel [49,50] the bond order is calculated to 2.12 (Cu(1)), 2.12 (Cu(2)), 1.94 (Cu(3)), and 1.90 (Cu(4)), respectively. Chiang et al. [51] reported on a similar hydroxo-bridged tetranuclear unit in a cobalt benzene-1,2,4,5-tetracarboxylate. The Cu²⁺-benzene-1,2,4,5-tetracarboxylate complex templated by 1,6-diaminohexane [47] shows similar polyhedra. The apical positions (O(11), O(13)) of the Cu(1) and Cu(3) polyhedra, however, in the present compound are more remote obviously due to hydrogen bonds with uncoordinated water molecules (see Tab. 3).

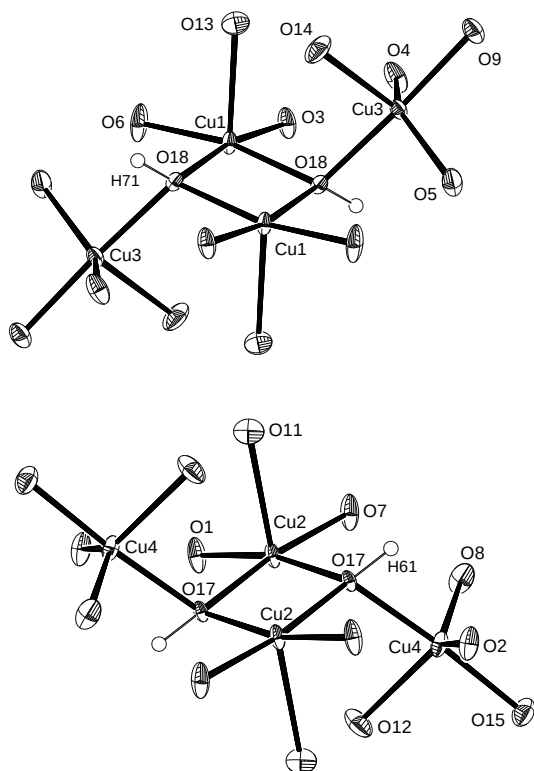


Figure 1. The coordination environments of Cu²⁺ (Ellipsoids are given at 50% probability, arbitrary radii for hydrogen atoms).

Table 1. The Coordination of Cu²⁺ in Cu₄(H₃N-(CH₂)₉-NH₃)(OH)₂[C₆H₂(COO)₄]₂·5H₂O

bond lengths (pm)			
Cu ₍₁₎ –O ₍₃₎	193.1(3)	Cu ₍₂₎ –O ₍₁₎	191.4(3)
Cu ₍₁₎ –O ₍₁₈₎	196.8(3)	Cu ₍₂₎ –O ₍₇₎	194.6(4)
Cu ₍₁₎ –O ₍₁₃₎	229.1(4)	Cu ₍₂₎ –O ₍₁₁₎	231.7(4)
Cu ₍₁₎ –O ₍₆₎	193.4(4)	Cu ₍₂₎ –O ₍₁₇₎	194.0(3)
Cu ₍₁₎ –O ₍₁₈₎ [#]	194.3(3)	Cu ₍₂₎ –O ₍₁₇₎ ^{#1}	197.1(3)
Cu ₍₁₎ ...Cu ₍₁₎ [#]	292.27(12)	Cu ₍₂₎ ...Cu ₍₂₎ ^{#1}	294.89(13)
Cu ₍₃₎ –O ₍₁₈₎	192.8(3)	Cu ₍₄₎ –O ₍₁₇₎	192.3(3)
Cu ₍₃₎ –O ₍₄₎	202.7(4)	Cu ₍₄₎ –O ₍₂₎	204.2(3)
Cu ₍₃₎ –O ₍₁₄₎	221.1(4)	Cu ₍₄₎ –O ₍₁₂₎	220.9(4)
Cu ₍₃₎ –O ₍₉₎	193.5(3)	Cu ₍₄₎ –O ₍₁₅₎	192.5(3)
Cu ₍₃₎ –O ₍₅₎	203.7(4)	Cu ₍₄₎ –O ₍₈₎	209.0(4)
bond angles (°)			
O ₍₃₎ –Cu ₍₁₎ –O ₍₆₎	86.1(2)	O ₍₁₎ –Cu ₍₂₎ –O ₍₇₎	88.7(2)
O ₍₆₎ –Cu ₍₁₎ –O ₍₁₈₎ [#]	95.77(14)	O ₍₁₎ –Cu ₍₂₎ –O ₍₁₇₎	92.66(14)
O ₍₆₎ –Cu ₍₁₎ –O ₍₁₃₎	168.1(2)	O ₍₇₎ –Cu ₍₂₎ –O ₍₁₇₎ ^{#1}	173.0(2)
O ₍₃₎ –Cu ₍₁₎ –O ₍₁₃₎	100.01(14)	O ₍₁₇₎ –Cu ₍₂₎ –O ₍₁₁₎	93.17(13)
O ₍₁₈₎ [#] –Cu ₍₁₎ –O ₍₁₃₎	89.86(13)	O ₍₁₇₎ ^{#1} –Cu ₍₂₎ –O ₍₁₁₎	95.78(13)
O ₍₁₈₎ –Cu ₍₁₎ –O ₍₁₃₎	95.31(13)	O ₍₁₎ –Cu ₍₂₎ –O ₍₁₇₎	167.0(2)
O ₍₆₎ –Cu ₍₁₎ –O ₍₁₃₎	96.5(2)	O ₍₁₇₎ –Cu ₍₂₎ –O ₍₇₎	95.08(14)
O ₍₃₎ –Cu ₍₁₎ –O ₍₁₈₎ [#]	169.7(14)	O ₍₁₇₎ –Cu ₍₂₎ –O ₍₁₇₎ ^{#1}	82.14(14)
O ₍₃₎ –Cu ₍₁₎ –O ₍₁₈₎	92.82(14)	O ₍₁₎ –Cu ₍₂₎ –O ₍₁₁₎	99.2(2)
O ₍₁₈₎ [#] –Cu ₍₁₎ –O ₍₁₈₎	83.29(14)	O ₍₇₎ –Cu ₍₂₎ –O ₍₁₁₎	90.8(2)
O ₍₁₈₎ –Cu ₍₃₎ –O ₍₉₎	175.71(14)	O ₍₁₇₎ –Cu ₍₄₎ –O ₍₂₎	88.11(14)
O ₍₉₎ –Cu ₍₃₎ –O ₍₄₎	91.9(2)	O ₍₁₇₎ –Cu ₍₄₎ –O ₍₈₎	92.01(14)
O ₍₉₎ –Cu ₍₃₎ –O ₍₅₎	89.2(2)	O ₍₂₎ –Cu ₍₄₎ –O ₍₈₎	138.8(2)
O ₍₁₈₎ –Cu ₍₃₎ –O ₍₁₄₎	87.83(14)	O ₍₁₅₎ –Cu ₍₄₎ –O ₍₁₂₎	86.9(2)
O ₍₄₎ –Cu ₍₃₎ –O ₍₁₄₎	116.4(2)	O ₍₁₇₎ –Cu ₍₄₎ –O ₍₁₅₎	174.5(2)
O ₍₁₈₎ –Cu ₍₃₎ –O ₍₄₎	90.70(14)	O ₍₁₅₎ –Cu ₍₄₎ –O ₍₂₎	96.4(2)
O ₍₁₈₎ –Cu ₍₃₎ –O ₍₅₎	90.90(14)	O ₍₁₅₎ –Cu ₍₄₎ –O ₍₈₎	86.7(2)
O ₍₄₎ –Cu ₍₃₎ –O ₍₅₎	142.3(2)	O ₍₁₇₎ –Cu ₍₄₎ –O ₍₁₂₎	87.75(14)
O ₍₉₎ –Cu ₍₃₎ –O ₍₁₄₎	87.9(2)	O ₍₂₎ –Cu ₍₄₎ –O ₍₁₂₎	129.6(2)
Cu ₍₃₎ –O ₍₁₈₎ –Cu ₍₁₎	113.6(2)	Cu ₍₄₎ –O ₍₁₇₎ –Cu ₍₂₎ ^{#1}	111.3(2)
Cu ₍₃₎ –O ₍₁₈₎ –Cu ₍₁₎ [#]	117.3(2)	Cu ₍₄₎ –O ₍₁₇₎ –Cu ₍₂₎	119.6(2)

#: -x;-y+1;-z+1, #1: -x;-y+1;-z

There are three crystallographically independent [C₆H₂(COO)₄]⁴⁻ anions (see Fig. 2 and 3). The anion I is almost planar with respect to the carbon skeleton. The largest deviation from a plane fitted to the carbon atoms is 4.5 pm (C(15)). The carboxylate groups are twisted against the C₆-ring by 38.8° ((C(16), O(1), O(2)), 56.0° ((C(17), O(3), O(4)), 36.1° ((C(18), O(5), O(6)), and 55.8° (C(19), O(7), O(8)), respectively. The C–O bond lengths range from 123.6(6) to 127.0(6) pm (Tab. 2). All oxygen atoms from this anion are involved in the Cu²⁺ coordination. The carbon skeletons of the centrosymmetric anions II and III are also planar with a largest out of plane deviation of 5.42 pm (C(22)) for anion II and 3.96 pm (C(27)) for anion III. The carboxylate groups show torsion angles of 26.4 (C(23), O(9), O(10)) and 65.1° (C(24), O(11), O(12)) for anion II as well as 70.2° (C(28), O(13), O(14)) and 22.6° (C(29), O(15), O(16)) for anion III with respect to the C₆-ring. The C–O bond lengths range from 122.1(6) to 129.4(6) pm. The shortest C–O bonds are formed by O(16) and O(10) which are not connected to Cu²⁺.

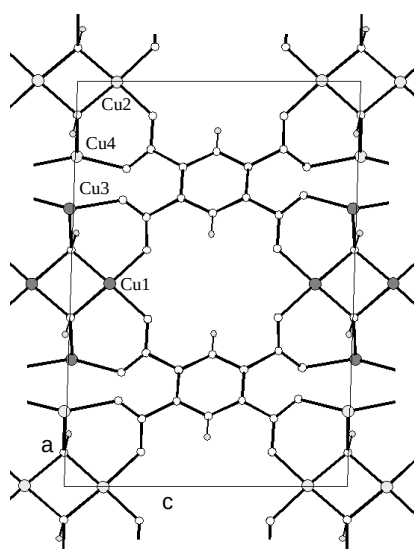


Figure 2. The connection between anion I and Cu^{2+} -cations.

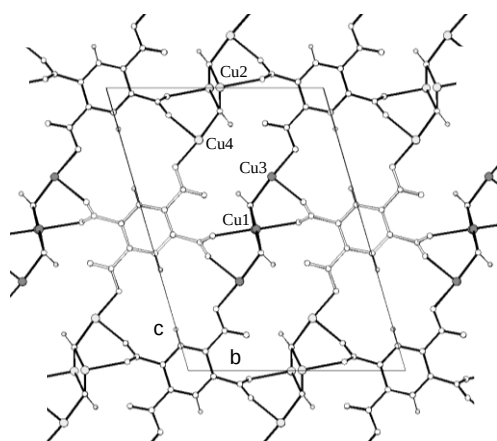


Figure 3. The connection between anions II and III and Cu^{2+} -cations (open bonds for anion III).

Table 2. Bond Lengths (pm) of the Benzene-1,2,4,5-tetracarboxylate-anions and the Nonane-1,9-diammonium-cation

Anion I					
$\text{C}_{(10)}\text{--}\text{C}_{(15)}$	139.4(7)	$\text{C}_{(10)}\text{--}\text{C}_{(16)}$	151.2(7)	$\text{O}_{(3)}\text{--}\text{C}_{(17)}$	127.0(6)
$\text{C}_{(10)}\text{--}\text{C}_{(11)}$	139.7(7)	$\text{C}_{(11)}\text{--}\text{C}_{(17)}$	151.2(7)	$\text{O}_{(4)}\text{--}\text{C}_{(17)}$	123.6(6)
$\text{C}_{(11)}\text{--}\text{C}_{(12)}$	139.7(7)	$\text{C}_{(13)}\text{--}\text{C}_{(18)}$	150.3(7)	$\text{O}_{(5)}\text{--}\text{C}_{(18)}$	124.8(6)
$\text{C}_{(12)}\text{--}\text{C}_{(13)}$	139.5(7)	$\text{C}_{(14)}\text{--}\text{C}_{(19)}$	151.1(7)	$\text{O}_{(6)}\text{--}\text{C}_{(18)}$	126.1(6)
$\text{C}_{(13)}\text{--}\text{C}_{(14)}$	140.0(7)	$\text{O}_{(1)}\text{--}\text{C}_{(16)}$	125.5(6)	$\text{O}_{(7)}\text{--}\text{C}_{(19)}$	126.7(6)
$\text{C}_{(14)}\text{--}\text{C}_{(15)}$	138.9(7)	$\text{O}_{(2)}\text{--}\text{C}_{(16)}$	125.7(6)	$\text{O}_{(8)}\text{--}\text{C}_{(19)}$	124.2(6)
Anion II					
$\text{C}_{(20)}\text{--}\text{C}_{(21)}$	140.8(7)	$\text{C}_{(20)}\text{--}\text{C}_{(23)}$	150.5(6)	$\text{O}_{(10)}\text{--}\text{C}_{(23)}$	122.2(6)
$\text{C}_{(21)}\text{--}\text{C}_{(22)}$	139.5(7)	$\text{C}_{(21)}\text{--}\text{C}_{(24)}$	150.2(7)	$\text{O}_{(11)}\text{--}\text{C}_{(24)}$	124.3(6)
$\text{C}_{(20)}\text{--}\text{C}_{(22)}$	138.9(7)	$\text{O}_{(9)}\text{--}\text{C}_{(23)}$	129.4(6)	$\text{O}_{(12)}\text{--}\text{C}_{(24)}$	127.7(6)
Anion III					

$\text{C}_{(25)}\text{--}\text{C}_{(27)}$	139.0(7)	$\text{C}_{(25)}\text{--}\text{C}_{(28)}$	151.0(7)	$\text{O}_{(14)}\text{--}\text{C}_{(28)}$	127.5(6)
$\text{C}_{(26)}\text{--}\text{C}_{(27)}$	138.7(7)	$\text{C}_{(26)}\text{--}\text{C}_{(29)}$	149.2(7)	$\text{O}_{(15)}\text{--}\text{C}_{(29)}$	129.3(6)
$\text{C}_{(26)}\text{--}\text{C}_{(25)}$	141.5(7)	$\text{O}_{(13)}\text{--}\text{C}_{(28)}$	124.1(6)	$\text{O}_{(16)}\text{--}\text{C}_{(29)}$	122.1(6)

Nonane-1,9-diammonium-cation

$\text{N}_{(1)}\text{--}\text{C}_{(1)}$	149.7(10)	$\text{C}_{(3)}\text{--}\text{C}_{(4)}$	153.9(11)	$\text{C}_{(6)}\text{--}\text{C}_{(7)}$	148.8(12)
$\text{N}_{(2)}\text{--}\text{C}_{(9)}$	148.4(11)	$\text{C}_{(2)}\text{--}\text{C}_{(3)}$	150.5(10)	$\text{C}_{(7)}\text{--}\text{C}_{(8)}$	151.5(11)
$\text{C}_{(1)}\text{--}\text{C}_{(2)}$	148.5(11)	$\text{C}_{(4)}\text{--}\text{C}_{(5)}$	146.1(11)	$\text{C}_{(8)}\text{--}\text{C}_{(9)}$	148.2(11)
$\text{C}_{(2)}\text{--}\text{C}_{(3)}$	150.5(10)	$\text{C}_{(5)}\text{--}\text{C}_{(6)}$	154.6(12)		

If the connection between Cu^{2+} and anion I is considered alone a two-dimensionally infinite arrangement parallel to the *ac*-plane results (Fig. 2). The same holds true with Cu^{2+} and anions II and III with respect to the *bc*-plane (Fig. 3). Thus the monodentate coordination between the benzene-1,2,4,5-tetracarboxylate anions and the Cu^{2+} -cations forms a three-dimensional framework with large channel-like voids along [001] (Fig. 4 and 5). The square-like crosssection of the channels has a diagonal of about 900 pm with the *van-der-Waals* radii [52] of the framework atoms taken into account. The channels accommodate water molecules not bound to Cu^{2+} and nonane-1,9-diammonium-cations compensating for the negative excess charge of the $\{(\text{Cu}_4(\text{OH})_2[\text{C}_6\text{H}_2(\text{COO})_4]_2)_n\}^{2n-}$ framework.

The skeleton of the nonane-1,9-diammonium-cation does not take a complete all-*trans* (antiperiplanar) conformation (Fig. 6a). The ammonium group $\text{N}(1)$ is rotated away which leads to a *gauche* conformation as seen in the *Newman* projection along the $\text{C}(2)\text{--}\text{C}(1)$ bond in Fig. 6b. The C--N bond lengths are 149.7(10) and 148.4(11) pm. The C--C bonds range from 146.1(11) pm to 154.6 (12) pm (Tab. 2). Such conformation was also found in e.g. nonane-1,9-diammonium bis-triiodide iodine [53] and catena-[catena- μ -(1,9-diaminononane)cadmium(II)tetra- μ -cyanonickelate(II)]-*o*-xylene(2/1) [54]. Whereas in $\text{NH}_3(\text{CH}_2)_9\text{NH}_3(\text{TiNbO}_5)_2$ [55] and in nonane-1,9-diammonium-chloride chloroacetate-hydroxyacetic acid [56] the diammonium-cations appear in the all-*trans* configuration.

The crystal structure is similar to the structure of a $\text{Cu}(\text{II})$ -benzene-1,2,4,5-tetracarboxylate templated by 1,6-diaminohexane, which crystallized in the space group $\text{P2}/c$ and exhibits also channels with a diagonal of approximately 900 pm [47]. However, using 1,4-diaminobutane [41] or 1,3-diaminopropane [40] as template agent the Cu^{2+} -cations and the $[\text{C}_6\text{H}_2(\text{COO})_4]^{2-}$ -anions build up different frameworks. In contrast to the nonane-1,9-diammonium-cations in the present structure the hexane-1,6-diammonium-, the butane-1,4-diammonium- and the propane-1,3-diammonium-cations adopt an all-*trans* conformation. In the case here the framework obviously determines the conformation of the template.

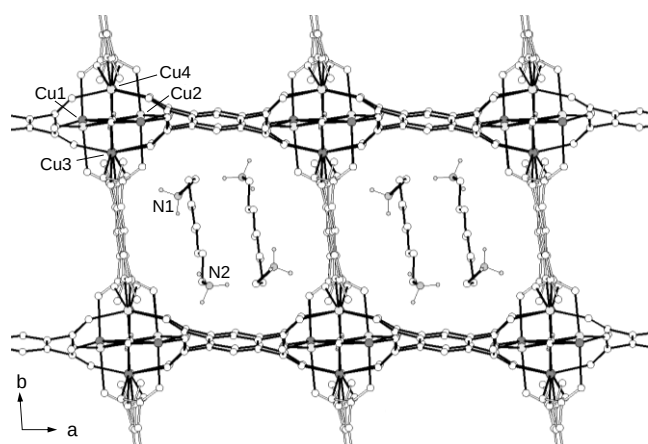


Figure 4. Crystal structure of $\text{Cu}_4(\text{H}_3\text{N}-(\text{CH}_2)_9-\text{NH}_3)(\text{OH})_2[\text{C}_6\text{H}_2(\text{COO})_4]_2 \cdot 5\text{H}_2\text{O}$ viewed along [001] showing the square-like channels. Anions II and III are drawn with open bonds (guest water molecules are omitted).

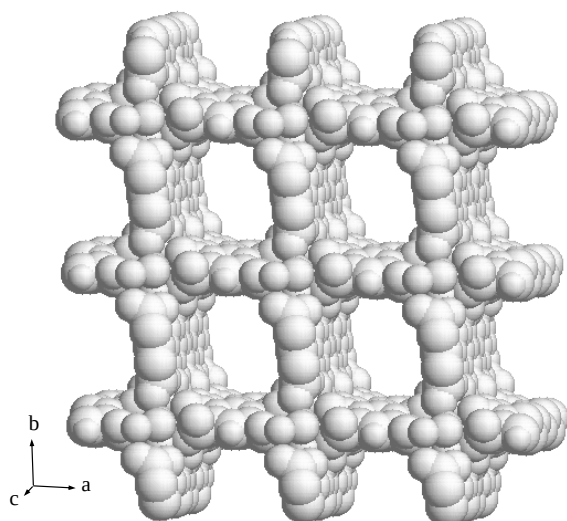


Figure 5. Space-filling model of the $\{\text{Cu}_4(\text{OH})_2[\text{C}_6\text{H}_2(\text{COO})_4]_2\}_n^{2n-}$ framework.

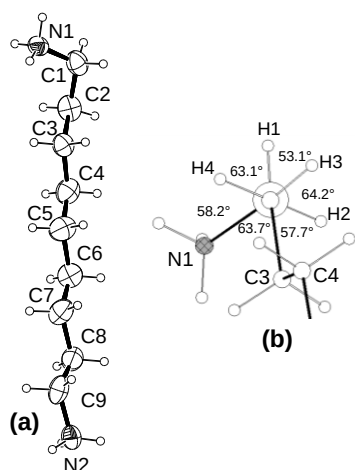


Figure 6. (a) The nonane-1,9-diammonium-cation (50 % probability ellipsoids, arbitrary radii for hydrogen atoms). (b) Newman projection along the C(2)–C(1) bond.

Table 3. Hydrogen bonds

N...O Distance (pm)			
$\text{N}_{(1)}-\text{H}_{(23)} \cdots \text{O}_{(w5)}$	288.1	$\text{N}_{(2)}-\text{H}_{(26)} \cdots \text{O}_{(3)}$	296.0
$\text{N}_{(1)}-\text{H}_{(24)} \cdots \text{O}_{(w1)}$	283.8	$\text{N}_{(2)}-\text{H}_{(27)} \cdots \text{O}_{(w3)}$	287.6
$\text{N}_{(1)}-\text{H}_{(25)} \cdots \text{O}_{(12)}$	276.8	$\text{N}_{(2)}-\text{H}_{(28)} \cdots \text{O}_{(w4)}$	272.3
O...O Distance (pm)			
$\text{O}_{(w1)}-\text{H}_{(31)} \cdots \text{O}_{(w2)}$	276.4	$\text{O}_{(w3)}-\text{H}_{(35)} \cdots \text{O}_{(14)}$	271.6
$\text{O}_{(w1)}-\text{H}_{(32)} \cdots \text{O}_{(9)}$	289.9	$\text{O}_{(w3)}-\text{H}_{(36)} \cdots \text{O}_{(w1)}$	287.5
$\text{O}_{(w2)}-\text{H}_{(33)} \cdots \text{O}_{(7)}$	300.1	$\text{O}_{(w4)}-\text{H}_{(38)} \cdots \text{O}_{(13)}$	276.5
$\text{O}_{(w2)}-\text{H}_{(34)} \cdots \text{O}_{(11)}$	277.3	$\text{O}_{(w5)}-\text{H}_{(39)} \cdots \text{O}_{(w3)}$	288.2
		$\text{O}_{(w5)}-\text{H}_{(40)} \cdots \text{O}_{(8)}$	308.7

The water molecules are not connected to Cu^{2+} and form hydrogen bonds to carboxylate oxygen atoms. However, not all carboxylate oxygen atoms are involved in hydrogen bonds. Surprisingly the carboxylate oxygen atoms ($\text{O}_{(10)}$ and $\text{O}_{(16)}$), which are not coordinated to Cu^{2+} do not appear in hydrogen bonds. This is a rather uncommon feature and is obviously accountable for the thermal stability of the dehydrated sample, as the uncoordinated carboxylate atoms do not suffer from structural destabilization by the cleavage of hydrogen bonds during the dehydration process. The water molecules $\text{O}_{(w1)}$, $\text{O}_{(w2)}$, $\text{O}_{(w3)}$ and $\text{O}_{(w5)}$ are linked together by hydrogen bonds. The nonane-1,9-diammonium-cation forms hydrogen bonds to the carboxylate oxygen atoms $\text{O}_{(3)}$ of anion I and $\text{O}_{(12)}$ of anion II and links the *ac*- and *bc*-plane of the $\{(\text{Cu}_4(\text{OH})_2[\text{C}_6\text{H}_2(\text{COO})_4]_2)_n^{2n-}\}$ framework. Additionally, except of $\text{O}_{(w2)}$ the diammonium-cation acts as proton donor to the water molecules (Tab. 3).

In the coordination polymer $\text{Cu}_2(\text{H}_3\text{N}-(\text{CH}_2)_6-\text{NH}_3)_{0.5}(\text{OH})[\text{C}_6\text{H}_2(\text{COO})_4] \cdot 3\text{H}_2\text{O}$ [47] in contrast to this the hydroxo groups and the carboxylate oxygen atoms, which are not connected to any Cu^{2+} -cations, are involved in strong hydrogen bonds. Moreover, the hexane-1,6-diammonium-cation forms only a hydrogen bond to the $[\text{C}_6\text{H}_2(\text{COO})_4]^{4-}$ anion in the *ac*-plane.

TGA/DTA studies (Fig. 7) were carried out in air from room temperature to 1000 °C at a heating rate of 10 K/min. An endothermic weight loss between 90 and 170 °C of 8.5% corresponds to the loss of all water molecules. (calc. 8.7%). The dehydrated sample was stable up to 260 °C. The complete decomposition process is finished at about 520 °C. The total weight loss is 69.0% (calc. 69.4%). The residue contained CuO and small amounts of Cu_2O which were identified by X-ray powder diffraction.

In $\text{Cu}_2(\text{H}_3\text{N}-(\text{CH}_2)_6-\text{NH}_3)_{0.5}(\text{OH})[\text{C}_6\text{H}_2(\text{COO})_4] \cdot 3\text{H}_2\text{O}$ [47] it turned out that the dehydrated sample is not thermally stable resulting in a continuous decomposition of the compound. The difference in the thermal behaviour between the present coordination polymer $\text{Cu}_4(\text{H}_3\text{N}-(\text{CH}_2)_9-\text{NH}_3)(\text{OH})_2[\text{C}_6\text{H}_2(\text{COO})_4]_2 \cdot 5\text{H}_2\text{O}$ and $\text{Cu}_2(\text{H}_3\text{N}-(\text{CH}_2)_6-$

$\text{NH}_3)_{0.5}(\text{OH})[\text{C}_6\text{H}_2(\text{COO})_4]\cdot 3\text{H}_2\text{O}$ can mainly be explained by the different hydrogen bonding modes.

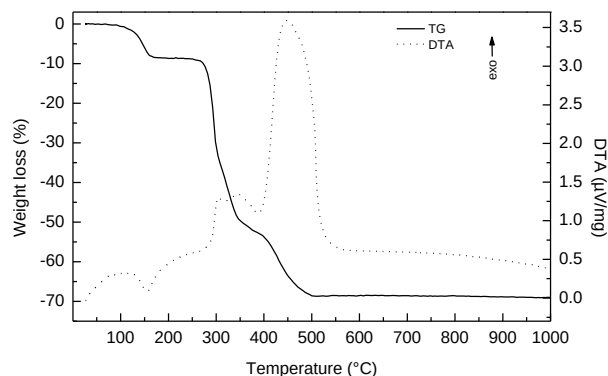


Fig. 7: Thermal analysis of $\text{Cu}_4(\text{H}_3\text{N}-(\text{CH}_2)_9-\text{NH}_3)(\text{OH})_2[\text{C}_6\text{H}_2(\text{COO})_4]_2\cdot 5\text{H}_2\text{O}$.

The IR spectrum is shown in Fig. 8. O–H and N–H stretching vibrations are in the range of 3000 to 3500 cm^{-1} . Sharp bands at 2923 and 2853 cm^{-1} reflect C–H stretching modes. The symmetrical and asymmetrical stretching vibration of the carboxylate groups appear at 1582 and 1367 cm^{-1} . The difference of 215 cm^{-1} indicates a monodentate coordination of the carboxylate groups [57]. The absorption band at 983 cm^{-1} is caused by the Cu–O–H bending mode [58].

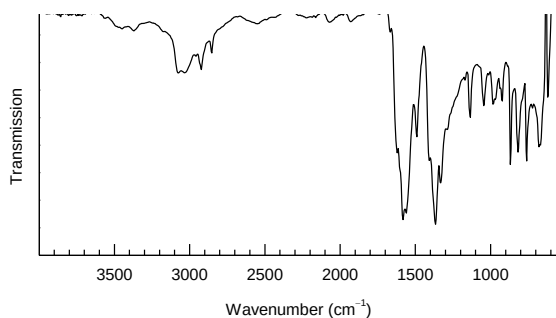


Fig. 8: IR spectrum of $\text{Cu}_4(\text{H}_3\text{N}-(\text{CH}_2)_9-\text{NH}_3)(\text{OH})_2[\text{C}_6\text{H}_2(\text{COO})_4]_2\cdot 5\text{H}_2\text{O}$.

tetracarboxylate-anions leads to a three-dimensional framework with negative excess charge and channel-like voids. The voids accommodate nonane-1,9-diammonium-cations as counter ions and water molecules, which are not connected to Cu^{2+} . The structure shows an interesting interaction between the template ion and the framework, resulting in a *gauche* conformation of one of the NH_3^+ -groups of the nonane-1,9-diammonium-cation. The template ion controls the formation and design of the framework and on the other hand the conformation of the template ion is simultaneously adapted to the framework.

Experimental Section

Single crystals of $\text{Cu}_4(\text{H}_3\text{N}-(\text{CH}_2)_9-\text{NH}_3)(\text{OH})_2[\text{C}_6\text{H}_2(\text{COO})_4]_2\cdot 5\text{H}_2\text{O}$ were synthesized in the presence of 1,9-diaminononane. An aqueous solution of 5ml $0.1\text{M Cu}(\text{NO}_3)_2$ was added to a solution of 5ml 0.2M 1,9-diaminononane. A precipitate, which appeared intermediately, was dissolved by addition of a small amount of 2M HNO_3 . Then a solution of 5ml 0.05M sodium benzene-1,2,4,5-tetracarboxylate and 0.2 g urea were added. The resulting solution was heated at 80°C for 3 days in a drying oven yielding turquoise parallelepipeds.

Results of elemental analysis: (molecular weight 1038.79) C 33.58 (calc. 33.53); H 3.88 (4.09); N 2.70 (2.60)%.

IR-ATR (cm^{-1}): $3445(\text{w})$, $3639(\text{w})$, $3075(\text{m})$, $3032(\text{w})$, $2923(\text{m})$, $2853(\text{m})$, $1582(\text{s})$, $1561(\text{s})$, $1491(\text{m})$, $1367(\text{s})$, $1333(\text{s})$, $1136(\text{m})$, $1045(\text{m})$, $983(\text{m})$, $924(\text{m})$, $867(\text{m})$, $817(\text{m})$, $761(\text{m})$, $678(\text{s})$, $620(\text{m})$.

ATR Fourier transformed infrared (IR-ATR) measurements were carried out at room temperature using a Bio-rad FTS 25. Thermoanalytic measurements were performed in flowing air using a Netzsch STA429 device. X-ray single crystal structure determination was performed on a Siemens P4 four-circle diffractometer (MoK α , graphite monochromator) in a theta range up to 25.00° . Numerical absorption corrections have been applied. The phase problem was solved by direct methods. Full matrix least squares refinement employing $|F|^2$ made use of the SHELXTL program suite [59]. Some of the hydrogen atoms have been placed into calculated positions, further hydrogen atom positions could be taken from Difference Fourier maps. They were allowed to refine with different common isotropic displacement parameters. Crystallographic data are given in Table 4.

Further details concerning the crystal structure analysis 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 992557.

Conclusions

In summary, we reported on the synthesis and crystal structures of a new Cu(II)-benzene-1,2,4,5-tetracarboxylate in the presence of 1,9-diaminononane as template agent. The connection between the Cu^{2+} -ions and the benzene-1,2,4,5-

Table 4. Crystallographic Data

Empirical formula	C ₂₉ H ₄₀ N ₂ Cu ₄ O ₂₃
Crystal system	triclinic
Space group	P-1 (no.2)
Lattice constants	a = 1057.5(2) pm b = 1166.0(2) pm c = 1576.7(2) pm α = 106.080(10)° β = 90.73(2)° γ = 94.050(10)°
Cell volume	1.8624(5) nm ³
Formulas in unit cell	2
Formula weight	1038.79 g/mol
Density (calc.)	1.852 g/cm ³
Wavelength	71.073 pm
Absorption coefficient	2.348 mm ⁻¹
Numerical absorption correction	min./max. transmittance 0.466/0.797
Temperature	293(2) K
Crystal size (mm)	0.10 x 0.36 x 0.50
F (000)	1056
Θ -range	2.32° – 25.00°
Limiting indices	h 0/+12; k -13/+13; l -18/+18
Reflections collected	6850
Independent reflections	6467 (R_{int} = 0.0165)
Structure solution	Direct methods
Structure refinement	Full-matrix least-squares on $ F ^2$
Refined parameters	582
Final mean shift/esd	0.002
Goodness-of-fit on $ F ^2$	1.307
Residuals (all data)	R_1 = 0.0544, wR_2 = 0.1093
Max. features in last difference Fourier synthesis	1076 and -616e-nm ⁻³

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