

## 1,3-Propanediammonium [ $\mu_4$ -1,2,4,5-benzenetetracarboxylato(4–)]copper(II) dihydrate with a microporous structure

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**Abstract:** Crystal structure analysis of the title complex,  $(\text{H}_3\text{NC}_3\text{H}_6\text{NH}_3)[\text{Cu}\{\text{C}_6\text{H}_2(\text{COO})_4\}] \cdot 2\text{H}_2\text{O}$ , showed that the structure is built up from Cu(II) and tetradentate 1,2,4,5-benzenetetracarboxylate(4–) (btc) ions forming a 3D open-framework with two different channels extending parallel to the [110]/[1,–1,0] and [001] directions. The first, wider channels accommodate 1,3-propanediammonium cations, whereas the second ones are filled with H<sub>2</sub>O molecules. The Cu(II) ions are in a tetrahedrally distorted square-planar environment consisting of four carboxylate O atoms from four different btc ligands. The four uncoordinated O atoms from the same carboxylate groups are placed around Cu(II) at longer distances ( $\approx 2.8$  Å), forming a distorted sphenoid. The complex crystallizes in the orthorhombic space group *Cc2m* with  $a = 8.887(1)$ ,  $b = 11.493(2)$ ,  $c = 16.457(3)$  Å,  $V = 1680.9(5)$  Å<sup>3</sup> and  $Z = 4$ . Final agreement indices are:  $R_1 = 0.0303$  for 1012 reflections with  $I > 2\sigma(I)$ ,  $wR_2 = 0.0493$  for 1317 independent reflections and 123 refined parameters. The compound was also characterized by IR spectroscopy and TG/DSC analysis.

**Keywords:** transition metal complexes, copper(II), 1,2,4,5-benzenetetracarboxylate ion, 1,3-propanediammonium ion, crystal structure, thermal properties.

### INTRODUCTION

The tetraanion of 1,2,4,5-benzenetetracarboxylic acid ( $\text{H}_4\text{btc}$ ), which is also known as pyromellitic acid, contains four COO groups and eight O atoms as potential donor sites. Two recent surveys of structural data<sup>1,2</sup> showed that bis-monodentate coordination of btc with only two *trans*-COO groups involved in the coordination is prevalent. However, more complicated manners of coordination are not uncommon. Thus, examples where btc participates in 12 coordination bonds to 10 transition metal atoms have also been described.<sup>1–3</sup> Since, as a rule, crystallo-

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graphic symmetry centre coincides with the centre of aromatic ring, btc always makes an even number of coordinative bonds.

When btc acts as a bis-monodentate ligand it greatly resembles the 1,4-benzenedicarboxylate(2-) ion building relatively simple binuclear<sup>4–6</sup> or 1D chain structures.<sup>7–10</sup> Double chains are characteristic for tetrakis-monodentate coordination,<sup>2,11–13</sup> but in this and other cases 2D layer<sup>14–19</sup> and 3D framework<sup>20–22</sup> structures are also found. This diversity results in very interesting structural motifs, which could be quite different in chemically similar or even identical systems.<sup>16</sup>

Most btc complexes contain a high number of coordinated and lattice water molecules, which together with carboxylate O atoms are involved in networks of hydrogen bonds. If aromatic amines are present as second ligands, face-to-face  $\pi$ - $\pi$  stacking interactions with interplanar distances between 3.26 and 3.90 Å are also observed.<sup>2,11,23</sup> Thus, btc complexes belong to so-called organic-inorganic hybrid materials, which are additionally stabilized by two types of interactions at the supramolecular level. All the described features classify btc complexes as very attractive from a fundamental and a practical point of view. As the only example, interesting low-temperature magnetic properties<sup>1,3,24</sup> caused by intra- and/or intermolecular magnetic exchange interactions between central atoms will be mentioned here.

This paper presents a continuation of our studies on transition metal complexes with anions of H<sub>4</sub>btc.<sup>4,7,25</sup> In relation to previous results, small modifications of the synthetic procedure resulted in a microporous (open framework) structure with 1,3-propanediammonium (trimethylenediammonium, H<sub>2</sub>tn<sup>2+</sup>) ions playing the role of template agent.

## EXPERIMENTAL

### *Preparation and characterization of the complex*

The infrared spectrum (KBr pellets) in the 4000–600 cm<sup>-1</sup> range was recorded on a Bomem MB-100 (Hartmann Braun) FTIR spectrophotometer. Thermal properties (25–1000 °C range) were investigated using a Q600 simultaneous DSC-TGA analyzer (TA Instruments). The heating rate and sample mass were 10 °C min<sup>-1</sup> and 5.66 mg, respectively. The furnace atmosphere consisted of dry nitrogen at a flow rate of 100 cm<sup>3</sup> min<sup>-1</sup>.

All reagents were commercial and used without further purification. A solution containing 0.750 g (0.004 mol) of Cu(NO<sub>3</sub>)<sub>2</sub> in 20 cm<sup>3</sup> of H<sub>2</sub>O was added dropwise into a clear aqueous solution (20 cm<sup>3</sup>) containing 0.33 cm<sup>3</sup> (0.004 mol) of tn and 0.51 g (0.002 mol) of H<sub>4</sub>btc. After 1 h of intensive mixing, the instantly formed turquoise blue precipitate, identified by chemical analysis as Cu<sub>2</sub>btc·7H<sub>2</sub>O, was removed by filtration. The pale blue mother liquor was left to evaporate and after approximately one week dark blue crystals suitable for crystal structure analysis were formed in a small yield. The complex is stable in air and insoluble in H<sub>2</sub>O and all common solvents. Calculated for C<sub>13</sub>H<sub>18</sub>CuN<sub>2</sub>O<sub>10</sub> (*M*<sub>r</sub> = 425.83): C 36.67, H 4.26, N 6.58 %. Found: C 36.75, H 4.27, N 6.61 %. Selected IR data (cm<sup>-1</sup>): 3480 (*s*), 3364 (*s*), 2980 (*vs,b*), 2900 (*vs,b*), 1598 (*vs*), 1570 (*vs*), 1528 (*vs,b*), 1480 (*s*), 1390 (*vs,b*), 1371 (*vs,b*), 1325 (*vs*), 1217 (*m*), 1198 (*m*), 1127 (*s*), 975 (*m*), 960 (*m*), 921 (*m*), 863 (*s*), 818 (*s*), 762 (*m*), 751 (*m*), 668 (*m*).

### *Crystal structure analysis*

An octahedron-like single crystal (dimensions: 0.22 × 0.13 × 0.09 mm) was chosen for room temperature (25 °C) data collection on a Bruker AXS four-circle diffractometer equipped with CCD

1K area detector and a flat graphite monochromator (MoK $\alpha$  radiation,  $\lambda = 0.71069$  Å). The crystal-to-detector distance and collimator size were 61.8 and 0.5 mm, respectively. Four sets of exposures as a combination of  $\omega$  and  $\varphi$  scans were used for data collection; each 20 s exposure covered an angular step of 0.3 ° giving an overall number of 1650 frames. The final unit cell parameters were determined from 1064 strong reflections with  $I > 10\sigma(I)$ . The software *SMART* was used for data collection, *SAINTE* for integration of the intensities, and *XPREP* (from *SHELXTL*) for empirical ( $\psi$ -scan) absorption correction (all Bruker AXS products).<sup>26</sup>

The structure was solved by direct methods (*SIR97*)<sup>27</sup> and refined on  $F^2$  by full-matrix least-squares (*SHELXL97*).<sup>28</sup> All non-hydrogen atoms were refined anisotropically. Crystal data and refinement results are listed in Table I.

TABLE I. Crystal data, data collection and refinement details

Chemical formula	C <sub>13</sub> H <sub>18</sub> CuN <sub>2</sub> O <sub>10</sub>
$M_r$	425.83
Crystal system, space group	Orthorhombic, <i>Cc2m</i> (No. 40)
$a$ (Å)	8.887(1)
$b$ (Å)	11.493(2)
$c$ (Å)	16.457(3)
$V$ (Å <sup>3</sup> )	1680.9(5)
$Z$	4
$F(000)$	876
$\mu$ (mm <sup>-1</sup> )	1.358
$\rho_x$ (g cm <sup>-3</sup> )	1.683
Range for data collection, $\theta$ (°)	3.81–26.39
Limiting indices ( $h, k, l$ ranges)	–4→10, –10→13, –20→20
Measured reflections	2828
Independent reflections	1317 [ $R_{\text{int}} = 0.0423$ ]
Observed reflections [ $I > 2\sigma(I)$ ]	1012
Refined parameters	123
$R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0301, wR_2 = 0.0581^\dagger$
$R$ indices (all data)	$R_1 = 0.0491, wR_2 = 0.0621^\dagger$
Flack parameter, <sup>29</sup> $x$	0.40(3)
Extinction coefficient, $k^\#$	0.0082(6)
Goodness-of-fit, $S$	0.935
$(\Delta/\sigma)_{\text{max}}$	0.004

$$^\dagger w = 1/[\sigma^2(F_o^2) + (0.0272P)^2], \text{ where } P = (F_o^2 + 2F_c^2)/3; \#F_c^* = kF_c[1+0.001F_c^2\lambda^3/\sin(2\theta)]^{-1/4}$$

During the refinement, the Flack parameter,  $x$ ,<sup>29</sup> was always about 0.4, indicating wrong absolute structure or presence of racemic twinning. After "inversion" of the structure, the Flack parameter  $x$  increased to about 0.6, confirming a twinned structure. Therefore, after all non-hydrogen atoms had been located and refined anisotropically, the refinement of racemic twinning was performed. The inclusion of twin improved the refinement and final ratio of twin components was 1.5:1. It is worth noticing that attempts to refine the structure in centrosymmetric space group *Ccmm* were ac-

accompanied by a disorder of  $\text{H}_2\text{tn}^{2+}$  ion and  $\text{H}_2\text{O}$  molecules showing that only part of the structure, *i.e.*, the 3D framework formed by btc and Cu(II) ions, has a centre of symmetry.

Hydrogen atoms (excluding those from  $\text{H}_2\text{O}$ ) were placed at calculated positions and refined using the riding model. The positions of water H atoms (H5A and H5B) were found in difference Fourier maps and refined isotropically with  $U_{\text{iso}} = 1.5U_{\text{eq}}(\text{O5})$ .

The highest ( $0.338 e \text{ \AA}^{-3}$ ) and the lowest ( $-0.242 e \text{ \AA}^{-3}$ ) residuals in the final  $\Delta F$  map were centred on  $\text{C}_4$  and  $\text{C}_2$ , respectively.

TABLE II. Atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}/\text{\AA}^2$
Cu	0.0000	0.0019(2)	0.0000	1.43(1)
O1	0.0156(4)	-0.1149(5)	0.0892(3)	2.0(1)
O2	0.2541(4)	-0.1165(4)	0.0492(3)	2.9(1)
O3	0.0289(5)	0.1155(5)	-0.0865(3)	2.2(1)
O4	0.2694(4)	0.1158(4)	-0.0507(3)	2.7(1)
O5	0.5513(3)	0.9154(4)	0.3903(2)	4.5(1)
N	-0.2694(5)	0.2359(5)	-0.1001(2)	2.8(1)
C1	0.1482(5)	-0.1543(5)	0.2500	1.7(3)
C2	0.1959(6)	-0.2038(6)	0.1749(4)	1.7(2)
C3	0.2053(6)	0.2013(6)	-0.1777(4)	1.4(2)
C4	0.1593(7)	0.1590(7)	-0.2500	1.5(3)
C5	0.1545(7)	-0.1430(6)	0.0985(4)	1.7(2)
C6	0.1658(7)	0.1402(6)	-0.0976(4)	1.7(2)
C7	-0.265(1)	0.2303(9)	-0.25000	1.8(2)
C8	-0.2855(5)	0.1618(5)	-0.1748(3)	3.0(1)

TABLE III. Selected bond distances (Å) and angles (°)

Cu–O1 (×2)	1.994(5)	O2–C5	1.238(7)
Cu–O3 (×2)	1.948(5)	O3–C6	1.263(6)
Cu–O2 (×2)	2.758(5)	O4–C6	1.234(7)
Cu–O4 (×2)	2.853(5)	C2–C5	1.48(1)
O1–C5	1.285(5)	C3–C6	1.53(1)
O1–Cu–O1 <sup>I</sup>	95.3(3)	O1–C5–O2	123.1(6)
O3–Cu–O3 <sup>I</sup>	95.8(3)	O1–C5–C2	117.2(6)
O1–Cu–O3 <sup>I</sup>	85.6(1)	O2–C5–C2	119.6(5)
O1 <sup>I</sup> –Cu–O3	85.6(1)	O3–C6–O4	125.2(6)
O1–Cu–O3	168.4(1)	O3–C6–C3	116.6(6)
O1 <sup>I</sup> –Cu–O3 <sup>I</sup>	168.4(1)	O4–C6–C3	118.1(5)

Symmetry code: (I)-x,y,-z

The final atomic coordinates and equivalent isotropic displacement parameters are listed in Table II with selected bond lengths and angles in Table III. The full list of bond distances and angles

together with atomic coordinates and their anisotropic displacement parameters has been deposited at the Cambridge Crystallographic Data Centre (see Supplementary materials).

## RESULTS AND DISCUSSION

### Crystal structure

In the first coordination sphere the Cu(II) ions are coordinated by four carboxylate O atoms (Fig. 1) from four different btc anions. The coordination geometry is a tetrahedrally distorted square-planar one, with the expected Cu–O distances (average: 1.97 Å) and angles (Table III). The other four O atoms from the same COO groups are placed around Cu(II) at longer distances (average: 2.81 Å), forming a distorted sphenoid. These contacts are slightly shorter than the sum of the van der Waals radii (2.92 Å)<sup>30</sup> and their importance is ambiguous. If the IR spectra are considered they look significant. Namely, the positions of the stretching COO vibrations,  $\nu_{\text{as}}(\text{COO})$  and  $\nu_{\text{s}}(\text{COO})$ , are found at 1528 and 1380 (mean value)  $\text{cm}^{-1}$ , respectively. The corresponding  $\Delta\nu$  value of 148  $\text{cm}^{-1}$  is small and when compared to the values for free  $\text{btc}^{4-}$  ions: 210  $\text{cm}^{-1}$  in  $\text{K}_4\text{btc}^{31}$  and 193  $\text{cm}^{-1}$  in  $\text{Na}_4\text{btc}$  (this study) indicates the presence of chelating COO groups.<sup>32,33</sup> On the other hand a similar  $\Delta\nu$  value (160  $\text{cm}^{-1}$ ) was already found in  $[\text{Ni}_2(\text{btc})(\text{en})_2(\text{H}_2\text{O})_6]\cdot 4\text{H}_2\text{O}$  (en = ethylenediamine), a complex containing only a combination of monodentate and uncoordi-

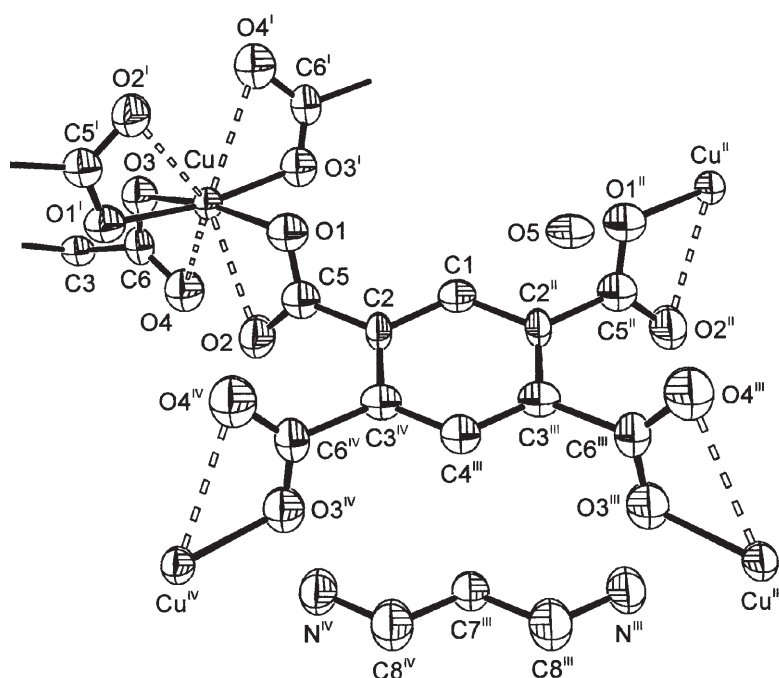


Fig. 1. Part of the structure with atomic numbering scheme and displacement ellipsoids at 80 % probability level (H atoms are omitted for clarity). Symmetry codes: (I)  $-x, y, -z$ ; (II)  $x, y, -z + 1/2$ ; (III)  $-x + 1/2, y - 1/2, z + 1/2$ ; (IV)  $-x + 1/2, y - 1/2, -z$ .

nated COO groups.<sup>4</sup> According to Deacon and Phillips<sup>32</sup> such behaviour can be explained by a "pseudo-bridging" arrangement of COO groups when they are involved in hydrogen bonding. The different length of O1–C5 and O2–C5, as well as of O3–C6 and O4–C6 bonds (Table III) also supports this explanation.

The btc anions are in special positions with two non-substituted ring C atoms (C1 and C4) on the mirror plane (Fig. 1). The aromatic ring is planar with deviations in the range 0.003(6) - 0.014(7) Å. However, two carboxylate C atoms, C5 and C6, are out of the plane of the aromatic ring by 0.135(6) and 0.166(7) Å, respectively. This can be attributed to the strain induced by polydentate coordination of the btc ligands. The dihedral angles between the COO groups and the aromatic ring are 48.9(9)° for C5/O1/O2 and 68.6(9)° for C6/O3/O4 group.

If the above-mentioned long Cu...O contacts are ignored, every btc ion acts as tetrakis-monodentate ligand bridging four Cu(II) ions (Fig. 1). In this way a 3D open-framework consisting of Cu(II) and btc ions connected through COO groups is produced (Fig. 2).

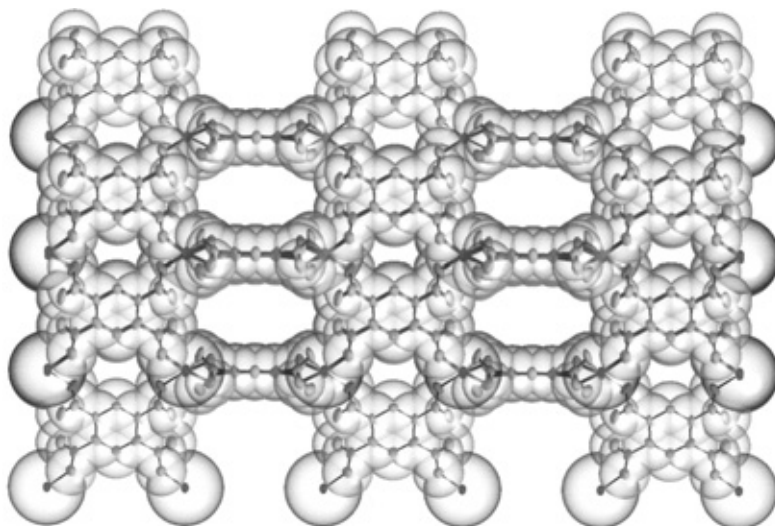


Fig. 2. A space-filling presentation of the structure projected along the [110] direction showing 3D Cu(II)-btc open framework and channels containing  $\text{H}_2\text{tn}^{2+}$  ions. (Lattice  $\text{H}_2\text{O}$  molecules,  $\text{H}_2\text{tn}^{2+}$  ions and H atoms are omitted for clarity.)

There are two orientations of the btc ligands with the dihedral angle between corresponding aromatic rings of 77.0(9)°. The Cu(II) ions are bridged by two btc ligands in one, and two btc ligands in the other orientation, with Cu(II)...Cu(II) distances of 7.264(1) and 8.229(1) Å alternatively.

The Cu(II)-btc framework has two sets of channels, which are large enough to accommodate species such as  $\text{H}_2\text{tn}^{2+}$  ions and  $\text{H}_2\text{O}$  molecules. The first, wider channels extend parallel to the [110]/[1,-1,0] directions and guest  $\text{H}_2\text{tn}^{2+}$  ions, which are oriented perpendicular to the channel axis. These channels have an elongated-octagonal

cross section with approximate dimensions of  $7 \times 3$  Å ( $\text{H}_2\text{tn}^{2+}$  ion is about 6.4 Å long) and occupy some 30 % of the unit cell volume. The second, narrower channels with effectively a rectangle cross section are parallel to the  $c$  axes. They are filled with  $\text{H}_2\text{O}$  molecules and represent about 10 % of the unit cell volume.

Due to the shape of the btc ligand and the relatively easy rotation of its COO groups,<sup>34</sup> rather remarkable cavities of different cross section are often found in corresponding complexes. In most cases the channel dimensions do not exceed 8 Å, but one example with channels of  $12.40 \times 7.20$  Å has been described.<sup>35</sup> Some channels are just hollow,<sup>2,9,11–13,19,36</sup> most of the remaining ones are filled by (sometimes disordered) lattice  $\text{H}_2\text{O}$  molecules.<sup>1,24,35</sup> Only in the complex  $\text{K}(\text{H}_3\text{O})[\text{Fe}_2(\text{btc})\text{F}_2] \cdot 3.5\text{H}_2\text{O}$  with octadentate btc ligands, small channels containing  $\text{K}^+$  and  $\text{H}_3\text{O}^+$  ions together with  $\text{H}_2\text{O}$  exist.<sup>20</sup>

To the best of our knowledge there are only several btc complexes containing protonated amines as counter ions. In a series of  $(\text{H}_2\text{pip})[\text{M}(\text{btc})(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$  complexes ( $\text{M} = \text{Co}, \text{Ni}$  and  $\text{Zn}$ ), piperazinium ( $\text{H}_2\text{pip}$ )<sup>37</sup> is present, whereas in  $(\text{H}_4\text{hpz})[\text{Co}_3(\text{btc})_2(\text{H}_2\text{O})_{12}] \cdot 11\text{H}_2\text{O}$  and  $(\text{H}_4\text{hpz})[\text{Co}(\text{btc})(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}$  homopiperazinium ( $\text{H}_4\text{hpz}$ ) dications are present.<sup>16</sup> All these compounds have 2D layered structures.

From the previous discussion, it follows that the here described complex is unique because it has a rigid 3D open framework structure with one of channels accommodating template  $\text{H}_2\text{tn}^{2+}$  ions.

TABLE IV. Geometry of hydrogen bonds

$D-H...A$	$d(D-H)/\text{Å}$	$d(H...A)/\text{Å}$	$d(D...A)/\text{Å}$	$D-H...A$	Symmetry code for $A$ atom
O5-H5A...O2	0.865(3)	2.187(4)	2.846(5)	132.8(2)	$x, y + 1, -z + 1/2$
O5-H5B...O4	0.801(4)	2.292(4)	2.965(6)	142.0(3)	$-x + 1, y + 1, z + 1/2$
N-H1A...O4	0.890	1.965	2.840(6)	167.1	$-x, y, -z$
N-H1B...O1	0.890	1.898	2.786(6)	175.1	$-x-1/2, y + 1/2, -z$
N-H1C...O5	0.890	1.971	2.836(6)	163.3	$-x + 1/2, y - 1/2, z - 1/2$

Lattice  $\text{H}_2\text{O}$  molecules and  $\text{H}_2\text{tn}^{2+}$  ions form hydrogen bonds with the COO groups. Except O3, all the O atoms are involved in a network of hydrogen bonds (Table IV), which can be described as infinite pseudo-chain extending along the  $c$  axes. The water O5 atom is a double H-donor toward O2 and O4, and a single H-acceptor from protonated  $\text{NH}_3^+$  group. The  $\text{NH}_3^+$  groups acts as a triple H-donor toward O1 and O4 atoms from btc and toward water O5 atom.

#### *Thermal properties and synthesis of the complex*

The complex dehydrates between 44 and 150 °C in a single step process. The mass loss is in accordance with the presence of two lattice  $\text{H}_2\text{O}$  molecules (found: 8.3, calcd.: 8.5 %). The anhydrous product is stable in the range 150–219 °C and decomposes in two partially overlapping steps. The first step (219–339 °C, DTG maximum: 286 °C) is more pronounced and corresponds to a mass loss of 52.5 %.

In the second step (339–458 °C, DTG maximum: 412 °C) an additional 8.9 % of mass are lost. Though the intermediate product obtained at about 460 °C was not characterized, its residual mass corresponds well to  $\text{CuCO}_3$  (found: 30.3, calcd.: 29.0 %). The decomposition continues further in a nearly horizontal step and the mass does not reach a constant value up to 1000 °C, where 20.7 % of residue is found. This is slightly higher than the theoretical values for  $\text{CuO}$  (18.7 %) and  $\text{Cu}_2\text{O}$  (16.8 %). All processes are endothermic.

The results of TG analysis may be rationalized in the following manner: Dehydration starts at a low temperature because the hydrogen bonds are weak (Table IV). The anhydrous complex  $(\text{H}_3\text{NC}_3\text{H}_6\text{NH}_3)[\text{Cu}\{\text{C}_6\text{H}_2(\text{COO})_4\}]$  is quite stable below 219 °C, meaning that it very likely retains its crystal structure and can be classified as a molecular sieve. However, the negatively charged  $\text{Cu}(\text{II})$ -btc framework cannot survive the removal of  $\text{H}_2\text{tn}^{2+}$  ions and further heating causes a collapse of the crystal lattice and decomposition of the compound.

Similar behaviour was found in the already mentioned  $(\text{H}_2\text{pip})[\text{M}(\text{btc})(\text{H}_2\text{O})_4]\cdot 4\text{H}_2\text{O}$  complexes,<sup>37</sup> which consist of negatively charged  $[\text{M}(\text{btc})(\text{H}_2\text{O})_4]_n$  layers with  $\text{H}_2\text{pip}^{2+}$  cations and  $\text{H}_2\text{O}$  molecules between them. The results of TG analysis and dehydration experiments<sup>37</sup> showed that the complexes can be dehydrated/rehydrated without loss of their original structure. However, the structure did not survive substitution of  $\text{H}_2\text{O}$  for  $\text{NH}_3$ . Unfortunately, because of the extremely small amount of crystals available it was not possible to check the structure of dehydrated product and the ionic exchange of  $\text{H}_2\text{tn}^{2+}$  ions in the present case.

The molar dehydration enthalpy,  $\Delta_{\text{deh}}H_{\text{m}}^{\circ}$ , calculated from the DSC curve is  $102.9 \text{ kJ mol}^{-1}$ . Since each  $\text{H}_2\text{O}$  molecule is involved in three hydrogen bonds (Table IV) and there are two  $\text{H}_2\text{O}$  molecules per formula unit, the mean energy of the hydrogen bonds is 17.2 kJ. This value is in excellent agreement with the value of 16 kJ obtained previously in a study of ternary transition metal complexes containing 1,4-benzenedicarboxylate ligands.<sup>38</sup>

The synthetic procedure used in this study deserves to be commented on in more detail. Most btc complexes are extremely insoluble in  $\text{H}_2\text{O}$  and other solvents. As a result of this, well-defined products and corresponding single crystals are usually prepared by hydrothermal (solvothermal) methods starting from  $\text{H}_4\text{btc}$  and its alkaline salts (see for example Refs. 1,2,9,11,21), or from  $\text{H}_4\text{btc}$  anhydride (see for example Refs. 14,39,40). Some ternary btc complexes are also prepared from solutions containing  $\text{M}^{n+}$  and  $\text{btc}^{4-}$  ions or  $\text{M}^{n+}$  ions and diamines, into which a solution of a second ligand is added.<sup>4,10,12–14,23</sup> The order used during the preparation of the title complex, *i.e.*, the neutralization of tn and  $\text{H}_4\text{btc}$  as a first step, suppresses a possible coordination of tn to  $\text{M}^{n+}$  ions. Thus, the present  $\text{H}_2\text{tn}^{2+}$  ions act as a template (structure-directing) agent. Such a role of organic amines and quaternary ammonium salts is well-known in the field of molecular sieve chemistry.<sup>41</sup> Therefore, this order of mixing seems to be a promising direction for future



syntheses of microporous compounds based on inorganic-organic hybrids. So far, some preliminary experiments with 1,2-ethanediamine and 1,2-propanediamine instead of 1,3-propanediamine were not successful. Inorganic porous materials are mainly based on  $MO_4$  tetrahedra ( $M = Si, Al, P, etc.$ ) and the size of the cavities is easily adjusted by the number of surrounding tetrahedra. Here, however, the size of the btc ion is fixed and its flexibility is limited, hence it is necessary to take into account the dimensions of the btc ion and the applied diamine, which, very likely should fit to each other.

*Supplementary materials.* Cambridge Crystallographic Data Centre, CCDC No. 260215 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)) A crystallographic Information File (CIF) is also available from authors upon request.

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## ИЗВОД

## 1,3-ПРОПАНДИАМОНИЈУМ

[ $\mu_4$ -1,2,4,5-БЕНЗЕНТЕТРАКАРБОКСИЛАТО(4-)]БАКАР(II) ДИХИДРАТ СА МИКРОПОРОЗНОМ СТРУКТУРОМДЕЈАН ПОЛЕТИ<sup>1</sup> и ЉИЉАНА КАРАНОВИЋ<sup>2</sup>

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Рендгенска структурна анализа наведеног комплекса  $(H_3NC_3H_6NH_3)[Cu\{C_6H_2(COO)_4\}] \cdot 2H_2O$ , показала је да тетрадентатни 1,2,4,5-бензентетракарбоксилат(4-) (btc) и Cu(II)-јони граде порозни 3D-скелет са две врсте канала који се пружају паралелно кристалографским правцима [110]/[1,-1,0] и [001]. Први, шири канали садрже 1,3-пропандиамонијум катјоне, док су други канали попуњени молекулима  $H_2O$ . Cu(II)-јони налазе се у тетраедарски деформисаном квадратно-планарном окружењу које се састоји од четири карбоксилатна O атома из четири различита btc-лиганда. Четири некоординирана O атома из истих карбоксилатних група налазе се око Cu(II) на дужем растојању ( $\approx 2.8 \text{ \AA}$ ) дајући неправилни сфеноид. Комплекс кристалише у ромбичној просторној групи  $Cc2m$  са  $a = 8,887(1)$ ,  $b = 11,493(2)$ ,  $c = 16,457(3) \text{ \AA}$ ,  $V = 1680,9(5) \text{ \AA}^3$  и  $Z = 4$ . Структурном анализом добијени су следећи индекси слагања:  $R_1 = 0,0303$  за 1012 рефлексја са  $I > 2\sigma(I)$ ,  $wR_2 = 0,0493$  за укупно 1317 независних рефлексја и 123 утачњавана параметра. Једињење је такође окарактерисано ИЦ-спектроскопијом и ТГ/ДСЦ анализом.

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