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**Synthesis of 1,2,4,5-Benzenetetrasulfonic Acid (H₄B₄S)
and its Implementation as a Linker for Building
Metal-Organic Frameworks on the Example of
[Cu₂(B₄S)(H₂O)₈] • 0.5 H₂O**

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Synthesis of 1,2,4,5-Benzenetetrasulfonic Acid (H₄B₄S) and its Implementation as a Linker for Building Metal-Organic Frameworks on the Example of [Cu₂(B₄S)(H₂O)₈] · 0.5 H₂O

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Dedicated to Professor Rüdiger Kniep on the Occasion of his 65th Birthday.

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Keywords: Copper Compounds; Crystal Structure; Metal-Organic Frameworks; Sulfonic Acids; Thermal Decomposition.

Abstract. Benzene 1,2,4,5-tetrasulfonic acid (H₄B₄S) was prepared in two steps starting from 1,2,4,5-Tetrachlorobenzene. Slow evaporation of an aqueous reaction mixture of H₄B₄S and Cu₂(OH)₂(CO₃) led to light green single crystals of [Cu₂(B₄S)(H₂O)₈] · 0.5 H₂O. X-ray single crystal investigations revealed the compound to be triclinic [*P*-1, *Z* = 1, *a* = 710.0(1), *b* = 713.7(1), *c* = 1077.1(2) pm, *α* = 98.41(2)°, *β* = 102.91(2)°, *γ* = 100.69(2)°]. In the crystal structure the Cu²⁺ ions are coordinated by four water molecules and two monodentate sulfonate anions yielding a tetragonally distorted [CuO₆] octahedron. The anions are connected to further copper ions leading to ladder shaped chains running along the [110] direction. According to DTA/TG investigations the dehydration of the compound is finished at 240°C and the decomposition of the anhydrous sulfonate starts at 340°C.

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Introduction

Metal organic frameworks (MOFs) [1] are three dimensional coordination polymers of knots (metal ions or metal-oxo clusters) and organic linker molecules. This class of porous materials has lately attracted attention, because of their potential applicability as catalysts or media for gas storage, in particular hydrogen [2]. Either neutral organic molecules or anions of di-, tri- or oligocarboxylic acids have been used as organic linkers between the knots. The variety of available carboxylic acids leads to a large number of known frameworks with tunable properties. The probably most famous example is the well known and so far most investigated MOF-5, which consists of $[Zn_4O]$ -clusters as knots linked by dianions of terephthalic acid (**1**) (Figure 1) [3]. Furthermore, the trianion of trimesic acid (**2**) plays an important role in the field of MOFs [4]. Many present and future applications of MOFs, in particular the use as hydrogen storage devices, require thermally stable frameworks. Thus, heat of sorption – as occurring during the charging of the materials – must not lead to a damage of the skeleton, and thermal processing of the compounds needs to be possible. The low stability of carboxylates towards heat is a significant disadvantage in this context, because it limits their applicability as linkers. For example, copper(II) terephthalate decomposes between 160–200°C under formation of carbon dioxide [5]. In order to prepare more thermally robust MOFs we decided to focus our research on sulfonate linkers as substitutes for the analogous carboxylate linkers. In contrast to the plethora of carboxylic acids, which are commercially available, most of the respective sulfonic acids must first be prepared, partly in complex reaction sequences. This is probably the reason why sulfonates as linkers in MOFs have so far rarely been reported [6]. Recently, we developed a convenient preparative route for the synthesis of benzenedi- and -trisulfonic acids *p*-H₂BDS (**4**) and H₃BTS (**5**) as analogues of terephthalic (**1**) and trimesic acid (**2**) making them available for building metal-organic frameworks [7]. Although we have not yet achieved to synthesize three-dimensional frameworks our investigations showed that the sulfonates possess indeed a remarkable thermal stability. Since Cu(II) [8] and Zn(II) [9] salts of tetracarboxylic acid **3** were also reported to give three-dimensional network structures, we decided to prepare the sulfo analogue of **3** being 1,2,4,5-benzenetetrasulfonic acid (H₄B4S) (**6**). To the best of our knowledge this acid has never been reported before. In extension of our previous work on copper salts of *p*-H₂BDS (**4**) and H₃BTS (**5**) we report herein the preparation of $[Cu_2(B4S)(H_2O)_8] \cdot 0.5 H_2O$ as the first salt of this acid **6**.

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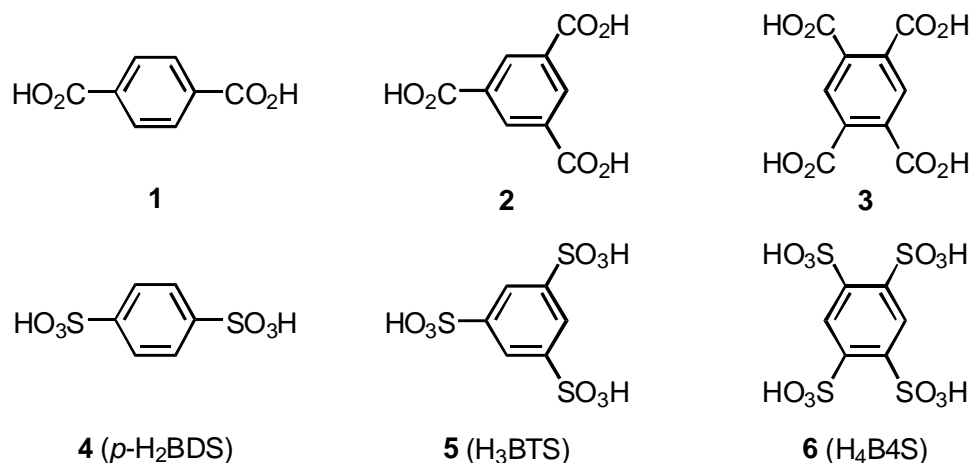


Figure 1. Carboxylic and sulfonic acids as linkers for metal-organic frameworks.

Experimental Section

General Information. All starting materials were commercially available and were used without further purification. ¹H- and ¹³C-NMR spectra were recorded on a Bruker Avance DRX 500 and Avance DPX 300. Multiplicities were determined with DEPT experiments. EI-MS and HRMS spectra were obtained with a Finnigan MAT 95 spectrometer, ESI-MS (HRMS) spectra with a Waters Q-TOF Premier. IR spectra were recorded on a Bruker Tensor 27 spectrometer equipped with a "GoldenGate" diamond-ATR unit. Thermal analyses (TG and DTA) were performed with a Mettler-Toledo SDTA 851e.

1,2,4,5-Tetramercaptobenzene (8). 1,2,4,5-Tetrachlorobenzene (**7**) (2.16 g, 10.0 mmol, 1.0 eq.) and NaSiPr (9.80 g, 100 mmol, 10 eq.) were suspended under an inert atmosphere (N₂) in *N,N*-dimethylacetamide (DMA) (40 ml) and the mixture was heated for 18 h to 100°C. Subsequently, Na (3.10 g, 135 mmol, 15.5 eq.) and more DMA (20 ml) were added under vigorous stirring. The resulting suspension was stirred for 16 h at 100°C. More Na (3.2 g, 139 mmol, 13.9 eq.) was then added and the mixture further stirred for 16 h at 100°C. If the conversion was incomplete (monitored by GLC), more Na (up to 2.5 g, 109 mmol, 10.9 eq.) and DMA (10 ml) could be added and the mixture further stirred for 5 h at 100°C. (For complete conversion the excess of sodium is mandatory; the reason for that observation is unknown yet). After cooling to ambient temperature, the mixture was carefully diluted with H₂O (200 ml) and *tert*-butylmethylether (MTBE) (150 ml) and acidified with conc. hydrochloric acid (until pH < 1). The layers were separated and the aqueous layer extracted with MTBE (2 x 100 ml). The combined organic layers were washed twice with H₂O (2 x 100 ml) and dried

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(MgSO₄). After filtration, the solvent was evaporated to give the crude product **8** as a brown solid. MeOH (150 ml) was added and the resulting suspension stirred for 0.5 h at ambient temperature. The solid was collected on a glas frit by suction, washed with MeOH (20 ml) and finally dried in high vacuum to give the title compound **8** (1.36 g, 6.59 mmol, 66%) as a light yellow solid, mp. 100–102°C. ¹H-NMR (500 MHz, CDCl₃): δ = 3.69 (s, 4H; S–H), 7.41 (s, 2H; 3,6-H) ppm. ¹³C{¹H}-NMR (125 MHz, CDCl₃): δ = 129.9 (4 C; C-1), 132.9 (2 CH; C-3) ppm. MS (EI, 70 eV): *m/z* (%) = 206 (100) [M⁺], 172 (25), 140 (15). IR (ATR): 3416 (m), 2922 (m), 2513 (s), 1427 (s), 1309 (s), 1252 (m), 1126 (s), 1068 (s), 931 (m), 860 (s), 616 (m) cm⁻¹. HRMS (EI, 70 eV): calcd. 205.9352 (for C₆H₆S₄), found 205.9347 [M⁺].

1,2,4,5-Benzenetetrasulfonic acid tetrahydrate (H₄B₄S · 4 H₂O) (6). Tetrathiole **8** (107 mg, 0.52 mmol, 1.0 eq.) was suspended in a mixture of MeOH (3.5 ml) and CHCl₃ (3.5 ml) while warming gently. H₂O₂ (30% in H₂O, 1.07 ml, 10.4 mmol, 20 eq.) was added. The suspension was stirred for 20 h at 23°C. Subsequently, H₂O (5 ml) was added and all volatile materials were removed in high vacuum. The residue was again suspended in H₂O (4 ml) and H₂O₂ (30% in H₂O, 1.07 ml, 10.4 mmol, 20 eq.) was added a second time. The suspension was further stirred for 16 h at 23°C. Subsequently, all volatile materials were removed in high vacuum to yield the title compound **6** (202 mg, 0.43 mmol, 83%) as a colorless solid, mp. 100°C. Thermal analysis (TG and DTA) showed this material to be the tetrahydrate. Caution: Vigorous exothermic decomposition was observed once during the final evaporation of volatile materials, when running the reaction on a 5 mmol scale. ¹H-NMR (300 MHz, D₂O): δ = 8.64 (s, 2 H; 3,6-H) ppm. ¹³C{¹H}-NMR (125 MHz, CD₃OD): δ = 132.8 (2 CH; C-3), 144.3 (4 C; C-1) ppm. MS (ESI, negative mode): *m/z* = 397 [M – H⁺], 198 [M – 2 H⁺], 132 [M – 3 H⁺]. IR (ATR): 3110 (m br), 2922 (m, br), 2852 (m, br), 2180 (w, br), 1701 (m, br), 1460 (m), 1136 (s), 1107 (s), 995 (s, br), 679 (s), 637 (s) cm⁻¹. HRMS (ESI, negative mode): calcd. 197.9303 (for C₆H₄S₄O₁₂²⁻), found 197.9298 [M – 2 H⁺]. C₆H₆S₄O₁₂ · 4 H₂O (470.42 g mol⁻¹).

[Cu₂(B₄S)(H₂O)₈] · 0.5 H₂O. Cu₂(OH)₂(CO₃) (70 mg, 0.317 mmol) was added to a solution of H₄B₄S · 4 H₂O (**6**) (147 mg, 0.312 mmol) in H₂O (10 ml). The resulting solution was stirred for 24 h at 50°C and then filtered. The greenish-blue filtrate was kept at ambient temperature and after a few days light green, plate shaped single crystals grew from the solution. They were collected by suction and dried under ambient conditions. For the X-ray investigation a small single crystal was glued onto a glass fibre and mounted on a image plate diffractometer (STOE IPDS I) and reflection intensities were collected at a temperature of 170 K. The struc-

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ture solution was successful with application of direct methods [10] and assuming the space group *P*-1. All non-hydrogen atoms were refined anisotropically using SHELXL97 [10]. The hydrogen atoms could be found in the difference fourier map and were refined without restraints. The data were numerically corrected for absorption effects [11]. The crystallographic data and their determination are summarized in the tables 1–4. CCDC 763273 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

DTA/TG measurements were performed with the help of a thermal analyzer (TGA/SDTA 851^E, METTLER-TOLEDO). For that purpose about 10 mg of the substance were filled into a corundum container and heated with a constant rate of 10 K min⁻¹ under flowing nitrogen. The thermal decomposition was monitored from 30°C up to 600°C. Characteristic points like onset and end temperatures of the thermal effects were taken from the differentiated DTA curve following common procedures using the software delivered with the analyzer [12].

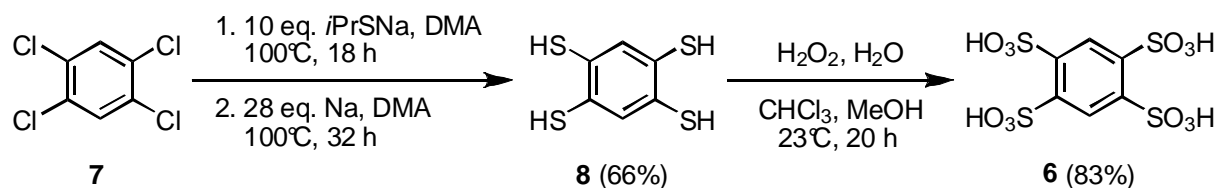
XRD investigations were performed with the help of the powder diffractometer STADI P (STOE) using a flat sample holder and Cu-K α_1 radiation.

Results and Discussion

Preparation of the sulfonic acid H₄B₄S. Aromatic sulfonic acids are commonly prepared by electrophilic aromatic substitution. However, a first sulfo substituent is deactivating the aromatic ring and moreover a *meta*-directing group, thus, a second or ever further substitutions are difficult to achieve and almost impossible in *ortho*- and *para*-positions. For this reason, we have decided to prepare the title tetrasulfonic acid **6** by oxidation of tetrathiol **8**. As the purification of the reaction product **6** was expected [7] to be very tedious, the use of hydrogen peroxide in a emulsion of water-methanol-chloroform was beneficial for this oxidation, because all other components of the reaction mixture could be removed in high vacuum after full conversion was achieved and the tetrasulfonic acid **6** as the only non-volatile material was obtained in high purity (Scheme 1). Thermal analysis (TG and DTA) showed this material to be the tetrahydrate. Tetrathiol **8** was prepared in a two-step one-pot protocol from tetrachlorobenzene **7**. First, a nucleophilic aromatic substitution with *i*PrSNa takes place in dimethylacetamide (DMA) under formation of the tetrathioether. Subsequently, an excess of so-

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dium is added to the reaction mixture and the isopropyl groups are reductively cleaved. Acidic workup afforded the product **8** in good yield.



Scheme 1. Synthesis of sulfonic acid H₄B₄S (**6**).

Structure of the Cu(II) Salt. To the best of our knowledge [Cu₂(B₄S)(H₂O)₈] · 0.5 H₂O is the first characterized salt of H₄B₄S (**6**). The compound crystallizes with triclinic symmetry (space group P-1, cf. Table 1) with the B₄S⁴⁻ anion being located on a center of inversion (C_i symmetry). Within the anion the phenyl ring is typically rigid with distances C–C around 140 pm and angles ∠C–C–C at about 120°. The distances C–S are 179.1(2) and 180.0(2) pm, respectively, and thus slightly longer than the distances observed for the 1,4-benzenedisulfonate anion (*p*-BDS²⁻) and the 1,3,5-benzenetrisulfonate anion (BTS³⁻) [7]. On the other hand, the bond length and angles within the sulfonate group fall in the same range (S–O: 145–147 pm, ∠O–S–O: 112–113°) as observed for the before mentioned anions. Each of the sulfonate groups of the B₄S⁴⁻ anion is connected to a Cu²⁺ ion. The latter are coordinated by two sulfonate groups of such as many B₄S⁴⁻ anions and four water molecules. The oxygen atoms of the anions are ion *trans* orientation within the resulting [CuO₆] octahedron with the distances Cu–O being 239.2(2) and 240.9(2) pm (Table 2). This is remarkably longer than the distances to the water oxygen atoms (Cu–O: 192.5–196.6 pm) but in accordance to the expected *Jahn-Teller* distortion for Cu²⁺. The linkage of the Cu²⁺ and the B₄S⁴⁻ ions leads to ladder-like chains that are oriented along the [100] direction of the unit cell (Figure 2). The connection might be expressed by ∞¹{[Cu(B₄S)_{2/4}(H₂O)_{4/1}]₂} according to *Niggli's* formalism. A similar ladder-type structure was observed for a copper salt of 1,2,3,5-tetracarboxylic acid (**3**) [8d]. In contrast to the sulfonate under discussion the latter contains no H₂O ligands but additional terpyridine molecules.

The ladder-type linkage leads to nearly rectangular voids as can be seen from the space filling representation in the right hand part of Figure 2. They have a dimension of about 710 x 495 pm² and incorporate disordered water molecules. The respective oxygen atom (O5) is located near to an inversion center and free refinement of the site occupation factor leads to a value of 0.5. The hydrogen atoms of this water molecule could not be detected with certainty. The water molecules in these voids are only held by weak hydrogen bonds. Between the

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$\infty^1\{[\text{Cu}(\text{B4S})_{2/4}(\text{H}_2\text{O})_{4/1}]_2\}$ chains medium strong hydrogen bonds are found with respect to the observed donor-acceptor distances (267–280 pm) and the angles (153–179°) within the hydrogen bridges (Table 5). The donors are water molecules that are coordinated to the Cu^{2+} ions while the oxygen atoms of the sulfonate groups act as acceptors.

The thermal dehydration of $[\text{Cu}_2(\text{B4S})(\text{H}_2\text{O})_8] \cdot 0.5 \text{H}_2\text{O}$ starts already at a temperature significantly below 100°C. With respect to the small endothermic signal and the mass loss of about 1.3% this first step can be attributed to the loss of the water molecules that are loosely bound in the voids of the ladder-type structure. The water molecules coordinated to the Cu^{2+} ions are released at higher temperature and the dehydration is completed at 240°C. The correlated mass loss of 21.6% is in perfect agreement with the calculated one (21.7%). The remaining anhydrous compound is stable up to 350°C, which points out the increased thermal stability of sulfonate type linkers compared to the respective carboxylates. According to XRD investigations of the obtained residue elemental copper is the only crystalline part of the decomposition product. However, if copper would be the only decomposition product, the observed mass loss should be 90.1%. The observed mass loss of 78.2% and the black colour of the residue suggest that also carbon may form in the reaction as an amorphous product. Further investigations must show, if the anhydrous compound can be gained in crystalline form to make a structure elucidation possible. Furthermore, the syntheses of new polysulfonic acids and the evaluation of their potential to build up thermally stable MOFs is our major goal.

Conclusion

Polycarboxyl acids are common linkers in metal organic frameworks. We have initiated a research program on preparation and utilization of polysulfonic acids with a similar substitution pattern as linkers in novel MOF type compounds in increased thermal stability. In this context we have developed a convenient route for the preparation of 1,2,4,5-Benzenetetrasulfonic acid ($\text{H}_4\text{B4S}$). Furthermore, a first salt of this acid, $[\text{Cu}_2(\text{B4S})(\text{H}_2\text{O})_8] \cdot 0.5 \text{H}_2\text{O}$, has been prepared. The compound exhibits a ladder like connection of copper ions an sulfonate linkers and can be dehydrated completely below 200°C. The anhydrous compound remains stable up to 350°C, proving the higher thermal stability of polysulfonates compared to their carboxylate analogues.

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11 12 13 14 **Figure Captions**

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17 **Figure 1.** Carboxylic and sulfonic acids as linkers for metal-organic frameworks.

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21 **Scheme 1.** Synthesis of sulfonic acid H₄B₄S (**6**).

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24 **Figure 2.** Ladder-shaped linkage of sulfonate linkers and copper ions according to
25 $\infty^1 \{[\text{Cu}(\text{B4S})_{2/4}(\text{H}_2\text{O})_4]_2 \cdot 0.5 \text{H}_2\text{O}\}$ in the crystal structure of $[\text{Cu}_2(\text{B4S})(\text{H}_2\text{O})_8] \cdot$
26 $0.5 \text{H}_2\text{O}$. The disordered water molecule (drawn in light blue) is located within
27 the open voids of the ladder. The right hand figure shows the ladder-shaped
28 chain in a space filling type (the disordered H₂O molecule is omitted).

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35 **Figure 3.** Arrangement of the chains shown in Figure 2 in the crystal structure of
36 $[\text{Cu}_2(\text{B4S})(\text{H}_2\text{O})_8] \cdot 0.5 \text{H}_2\text{O}$ viewed along [010].

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41 **Figure 4.** Linkage of the ladder-shaped chains by hydrogen bonds (dotted lines). The
42 crystal structure is shown along the [100] and the [010] direction, respectively
43 (disordered water molecules are omitted).

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48 **Figure 5.** DTA/TG diagram of $[\text{Cu}_2(\text{B4S})(\text{H}_2\text{O})_8] \cdot 0.5 \text{H}_2\text{O}$.

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Table 1. [Cu₂(B₄S)(H₂O)₈] · 0.5 H₂O. Crystallographic data and their determination

lattice parameters	$a = 710.0(1)$ pm
	$b = 713.7(1)$ pm
	$c = 1077.1(2)$ pm
	$\alpha = 98.2^\circ(2)$
	$\beta = 102.1^\circ(2)$
	$\gamma = 100.9^\circ(2)$
cell volume	512.6(1) Å ³
density (calcd.)	2.156 g cm ⁻³
no. of formula units	1
crystal system	triclinic
space group	<i>P</i> -1 (Nr. 2)
measuring device	Stoe IPDS I
radiation	Mo-K α (graphite monochromator, $\lambda = 71.07$ pm)
temperature	153.0 K
θ -range	$5.92^\circ < 2\theta < 56.5^\circ$
φ -range; φ -increment	$0.0^\circ < \varphi < 320.4^\circ$; 2.0°
index range	$-9 \leq h \leq 9$
	$-9 \leq k \leq 9$
	$-14 \leq l \leq 14$
no. of images	160
exposure time	2.5 min
detector distance	60 mm
absorption correction	numerical, after optimization of crystal shape
μ	25.79 cm ⁻¹
no. of measured reflections	8147
no. of unique reflections	2340
no. of observed reflections with	1944
$I_o > 2\sigma(I_o)$	
R_{int} ; R_σ	0.0361; 0.0330
programs	SHELXS97 and SHELXL97
scattering factors	Intern. Tables, vol. C [13]
goodness of fit (all data)	1.024

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goodness of fit ($I_0 > 2\sigma(I_0)$)	1.024
R1; wR2 ($I_0 > 2\sigma(I_0)$)	0.0247; 0.0606
R1; wR2 (all data)	0.0305; 0.0616
max./min. residual electron density	0.537 / $-0.516 \text{ e } \text{\AA}^{-3}$

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Table 2. Atomic positions and equivalent isotropic displacement factors for $[\text{Cu}_2(\text{B}_4\text{S})(\text{H}_2\text{O})_8] \cdot 0.5 \text{H}_2\text{O}$.

Atom ^{a)}	x/a	y/b	z/c	$U_{\text{eq}} / \text{\AA}^2$ ^{a)}
Cu1	0.34730(4)	0.17999(4)	0.65762(2)	0.01213(9)
O1	0.3237(3)	0.1355(3)	0.8299(2)	0.0182(4)
H11	0.222(6)	0.098(5)	0.831(3)	0.027 ^{b)}
H12	0.413(5)	0.082(5)	0.865(3)	0.027
O2	0.2121(4)	0.9151(3)	0.5793(2)	0.0283(5)
H21	0.204(6)	0.831(6)	0.617(4)	0.043
H22	0.175(6)	0.878(6)	0.528(4)	0.043
O3	0.3567(3)	0.2298(2)	0.4842(2)	0.0167(3)
H31	0.274(5)	0.289(5)	0.450(3)	0.025
H32	0.340(5)	0.139(5)	0.434(3)	0.025
O4	0.4999(3)	0.4459(2)	0.7350(2)	0.0197(4)
H41	0.446(5)	0.519(5)	0.744(3)	0.029
H42	0.589(6)	0.467(5)	0.707(3)	0.029
S1	0.01263(8)	0.47232(7)	0.70402(5)	0.0098(1)
O11	0.0442(2)	0.2833(2)	0.6525(1)	0.0125(3)
O12	0.1821(3)	0.6295(2)	0.7136(2)	0.0172(3)
O13	0.8249(2)	0.5068(2)	0.6350(2)	0.0154(3)
C1	0.0012(3)	0.4741(3)	0.8686(2)	0.0097(4)
C2	0.9055(3)	0.3199(3)	0.9158(2)	0.0094(4)
S2	0.78382(8)	0.07801(7)	0.82652(5)	0.0095(1)
O21	0.6669(2)	0.0984(2)	0.7001(1)	0.0124(3)
O22	0.6590(2)	0.9981(2)	0.9047(2)	0.0142(3)
O23	0.9393(2)	0.9762(2)	0.8134(2)	0.0152(3)
C3	0.9076(3)	0.3502(3)	0.0466(2)	0.0112(4)
H1	0.844(4)	0.248(4)	0.073(3)	0.013
O5 ^{c)}	0.532(2)	0.549(2)	0.971(1)	0.057(3)

$$U_{\text{eq}} = 1/3 [U_{11}(\text{aa}^*)^2 + U_{22}(\text{bb}^*)^2 + U_{33}(\text{cc}^*)^2 + 2 U_{12} \text{aba}^*\text{b}^*\cos \gamma + 2 U_{13} \text{aca}^*\text{c}^*\cos \beta + 2 U_{23} \text{bcb}^*\text{c}^*\cos \alpha] [14]$$

^{a)} all atoms are located on the Wyckoff site $2i$ ^{b)} isotropic displacement parameters for H atoms^{c)} half occupied site

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Table 3. Selected internuclear distances/pm for $[\text{Cu}_2(\text{B}_4\text{S})(\text{H}_2\text{O})_8] \cdot 0.5 \text{H}_2\text{O}$.

Cu1–O1	196.6(2)
Cu1–O2	192.5(2)
Cu1–O3	196.5(2)
Cu1–O4	196.0(2)
Cu1–O11	239.2(2)
Cu1–O21	240.9(2)
S1–O11	145.9(2)
S1–O12	145.9(2)
S1–O13	145.7(2)
S1–C1	179.1(2)
S2–O21	147.1(2)
S2–O22	145.2(2)
S2–O23	145.0(2)
S2–C2	180.0(2)
C1–C2	140.5(3)
C1–C3	138.8(3)
C2–C3	139.0(3)

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Table 4. Selected angles/° for [Cu₂(B₄S)(H₂O)₈] · 0.5 H₂O.

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6	O1–Cu1–O2	91.2(1)
7	O1–Cu1–O4	90.1(1)
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9	O1–Cu1–O11	82.6(1)
10		
11	O1–Cu1–O21	89.7(1)
12		
13	O2–Cu1–O3	89.0(1)
14		
15	O2–Cu1–O11	93.1(1)
16		
17	O2–Cu1–O21	92.4(1)
18		
19	O3–Cu1–O4	89.8(1)
20		
21	O3–Cu1–O11	94.1(1)
22		
23	O3–Cu1–O21	93.6(1)
24		
25	O4–Cu1–O11	90.4(1)
26		
27	O4–Cu1–O21	84.4(1)
28		
29	O1–Cu1–O3	176.7(1)
30		
31	O2–Cu1–O4	176.5(1)
32		
33	O11–Cu1–O21	170.7(1)
34		
35	O11–S1–O12	111.8(1)
36		
37	O11–S1–O13	112.6(1)
38		
39	O12–S1–O13	113.1(1)
40		
41	C1–S1–O11	107.6(1)
42		
43	C1–S1–O12	104.5(1)
44		
45	C1–S1–O13	106.7(1)
46		
47	O21–S2–O22	112.1(1)
48		
49	O21–S2–O23	112.1(1)
50		
51	O22–S2–O23	113.6(1)
52		
53	C2–S2–O21	106.9(1)
54		
55	C2–S2–O22	104.9(1)
56		
57	C2–S2–O23	106.6(1)
58		
59	S1–C1–C2	126.3(2)
60		
	S1–C1–C3	114.6(2)
	C2–C1–C3	119.0(2)
	S2–C2–C1	127.2(2)
	S2–C2–C3	114.6(2)
	C1–C2–C3	118.2(2)

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C1-C3-C2	122.8(2)
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Table 5. Observed hydrogen bonds in $[\text{Cu}_2(\text{B}_4\text{S})(\text{H}_2\text{O})_8] \cdot 0.5 \text{H}_2\text{O}$.

D-H	d(D-H) / pm	d(H...A) / pm	$\angle\text{DHA} / ^\circ$	d(D...A) / pm	A
O1-H11	72	199	173.7	271	O23
O1-H12	85	193	160.8	274	O22
O2-H21	78	189	178.5	267	O12
O2-H22	56	221	164.4	274	O11
O3-H31	84	199	157.3	278	O13
O3-H32	75	205	172.6	279	O21
O4-H41	71	214	153.4	280	O12
O4-H42	76	199	176.6	275	O13

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Table 6. DTA/TG data for the decomposition of $[\text{Cu}_2(\text{B}_4\text{S})(\text{H}_2\text{O})_8] \cdot 0.5 \text{H}_2\text{O}$.

Stage	$T_{\text{onset}} / ^\circ\text{C}$	$T_{\text{end}} / ^\circ\text{C}$	$T_{\text{max}} / ^\circ\text{C}$	Mass loss obs.	Mass loss calcd.
1. loss of 1/2 equivalents of H_2O	– ^{a)}	– ^{a)}	50	1.3%	1.4%
2. loss of eight equivalents of H_2O	101	203	152	21.6%	21.7%
3. decomposition of the organic ligands	348	422	384	78.2%	– ^{b)}

^{a)} values cannot be determined with certainty;

^{b)} calculation not possible due to unknown content of carbon in the residue

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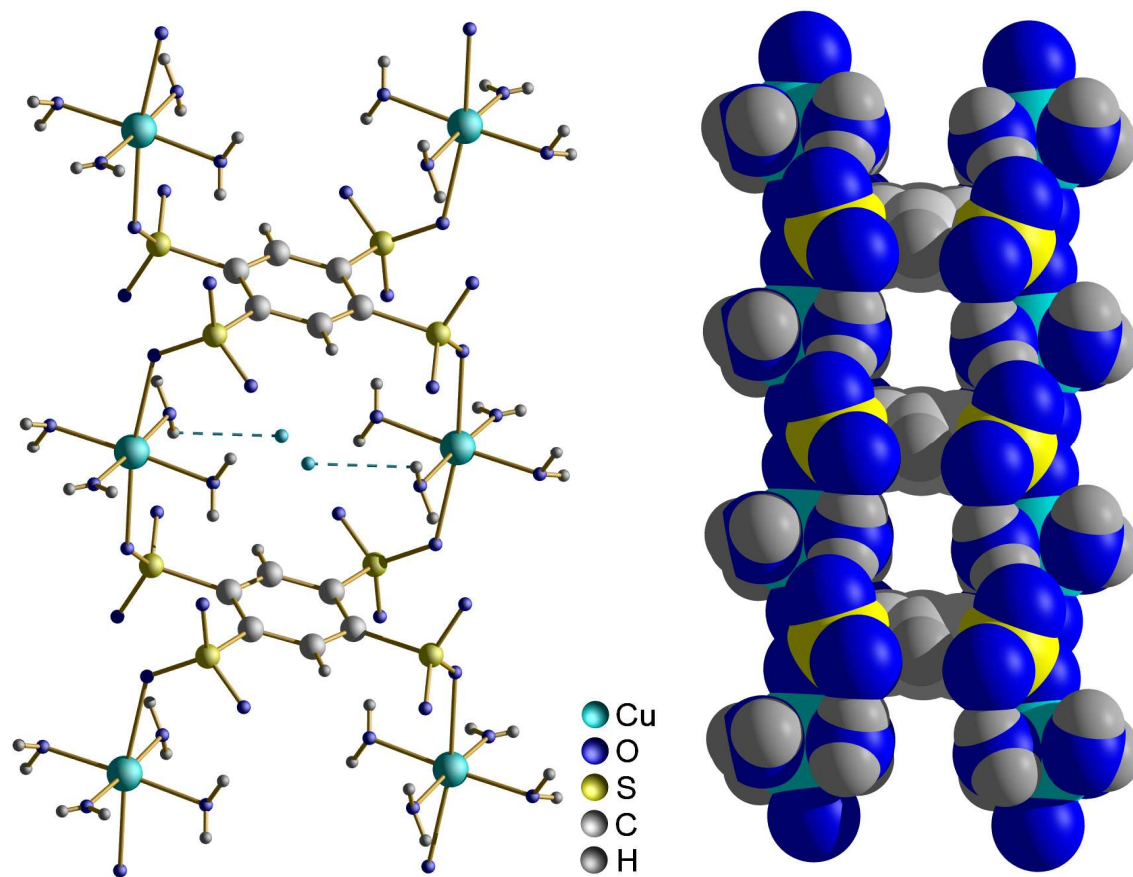


Figure 2.

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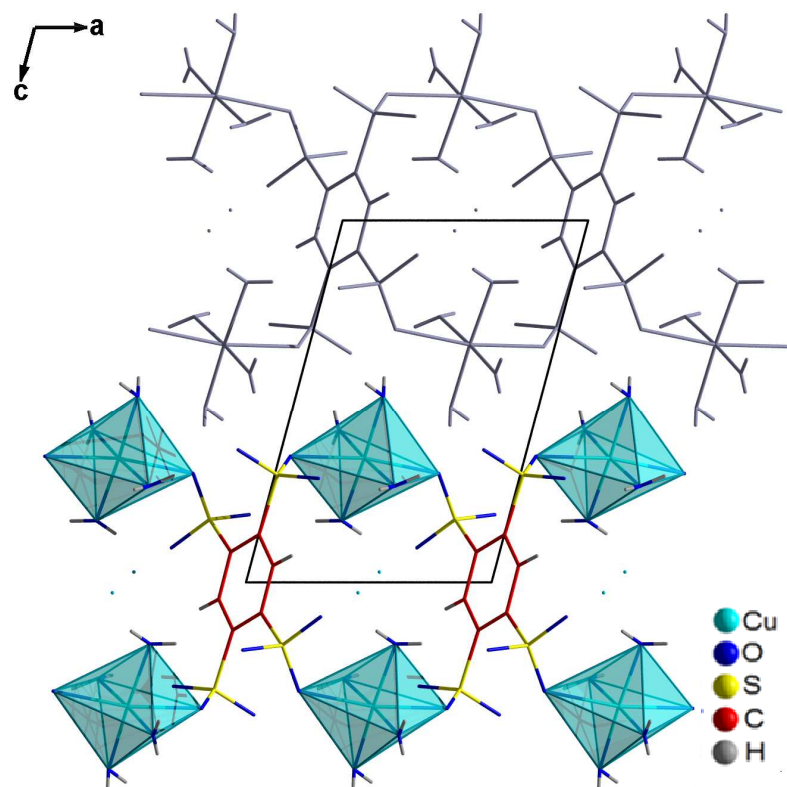


Figure 3.

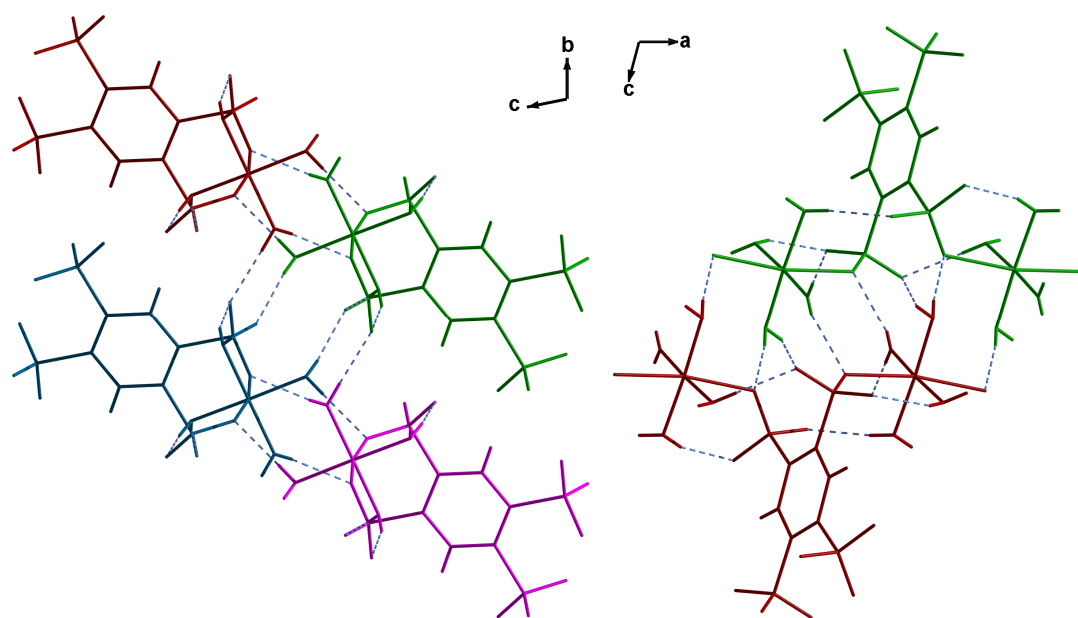


Figure 4.

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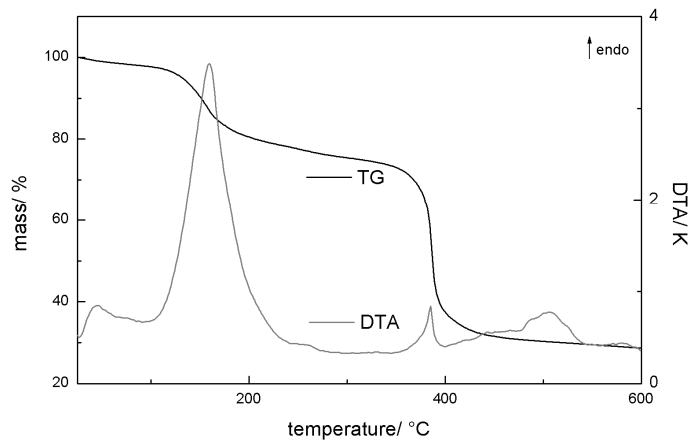


Figure 5.