DOI: 10.1002/ejic.200900914

Sulfonic Acid Analogs of Terephthalic and Trimesic Acid as Linkers in Metal-Organic Frameworks – Synthesis of Thermally Robust MOFs

Andrea Mietrach,[a] Thomas W. T. Muesmann,[a] Jens Christoffers,*[a] and Mathias S. Wickleder*[a]

Keywords: Aromatic substitution / Copper / Metal-organic frameworks / Sulfonic acids / Thermal analysis

p-Benzenedisulfonic acid and 1,3,5-benzenetrisulfonic acid are prepared in an efficient and scalable two-step protocol from respective bromobenzene derivatives. These acids are used in analogy to terephthalic and trimesic acid for the formation of metal-organic frameworks with copper(II) centers. Due to the enhanced acidity of sulfonic acids, weakly basic malachite can be used as inorganic precursor material. After dehydration at about 100 °C, the anhydrous frameworks exhibit significantly increased thermal stability (up to 400 °C) relative to the commonly known carboxylate MOFs.

Introduction

Metal-organic frameworks (MOF)[1] are porous materials, which lately attracted attention because of their potential applicability as catalysts or media for gas storage, in particular hydrogen.[2] Either neutral molecules or anions of di-, tri- or oligocarboxylic acids are used as organic linkers between the knots (metal ions or metal-oxo clusters). The variety of available carboxylic acids leads to a large number of known frameworks with tunable properties. One 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 benzenetricarboxylic acid (**2**) plays an important role in the field of MOFs.[4] Many present and future applications of MOFs, in particular their use as hydrogen storage devices, require thermally stable frameworks. Thus, heat of sorption, which is produced 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 and 200 °C with formation of carbon dioxide.[5]

In the present work, we have developed a convenient preparative route for the synthesis of di- and trisulfonic acids for the use instead of the analogous carboxylates in the preparation of more stable MOFs. Investigations on the thermal stability of salts from *m*-benzenedisulfonic acid (**3**) have shown that these materials are stable up to 400 °C;[6] structural investigations on such compounds have, however, not been made so far. Di- and trisulfonates as linkers in MOFs have so far rarely been reported.[7] This might be due to the lack of availability of sulfonic acids with substitution patterns similar to the carboxylic acids used in MOFs. While *m*-disulfonic acid **3** is commercially available as its sodium salt, no efficient and scalable procedures exist for the preparation of *p*-disulfonic acid **4** or 1,3,5-trisulfonic acid **5**.

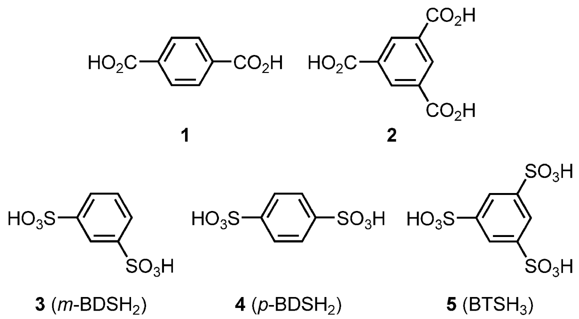

Figure 1. Carboxylic and sulfonic acids as linkers for metal-organic frameworks.

Results and Discussion

Preparation of Sulfonic Acids

The synthesis of organic oligosulfonic acids is limited by the regioselectivity as well as the deactivating nature of sulfo groups. Therefore, we have decided to oxidize dithiol **7** in order to prepare 1,4-disulfonic acid **4**, the sulfo analog of terephthalic acid (**1**). As the purification of reaction product **4** turned out to be very tedious, the use of hydrogen

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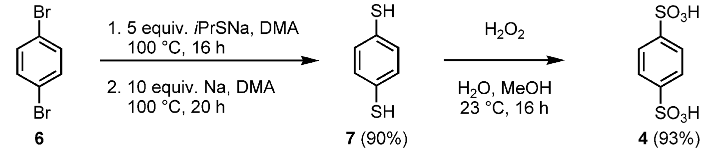
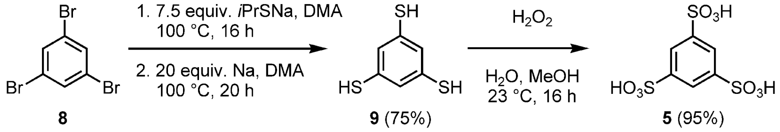
[a] Institut für Reine und Angewandte Chemie, Carl von Ossietzky-Universität Oldenburg,
26111 Oldenburg, Germany
Fax: +49-441-798-3873
E-mail: jens.christoffers@uni-oldenburg.de





Scheme 1. Synthesis of sulfonic acids *p*-$BDSH_2$ (**4**) and $BTSH_3$ (**5**).

peroxide in a mixture of water and methanol was beneficial for the oxidation of dithiol **7**. All other components of the reaction mixture could be removed in high vacuum after full conversion was achieved, and disulfonic acid **4** as the only nonvolatile material was obtained in high purity (Scheme 1). Trisulfonic acid **5** was prepared from trithiol **9** in the same manner. Dithiol **7**[8] and trithiol **9**[9] have been prepared before by multi-step procedures, which are not suitable for up-scaling. We herein report on a sequential one-pot protocol for the synthesis of both intermediates **7** and **9** from bromobenzenes **6** and **8**. First, a nucleophilic aromatic substitution with *i*PrSNa takes place in dimethylacetamide (DMA) with formation of the dithioether and trithioether, respectively. Subsequently, an excess of sodium is added to the reaction mixture and the isopropyl groups are reductively cleaved. Acidic workup afforded the products **7** and **9** in good yields.

Copper *m*-Disulfonate

Our first study on a framework structure was accomplished by conversion of *m*-benzenedisulfonic acid (**3**, *m*-$BDSH_2$) (prepared from its commercially available sodium salt) with basic copper carbonate $Cu_2(OH)_2(CO_3)$ (malachite) in aqueous solution. The copper salts crystallized as the hexahydrate $[Cu(m\text{-}BDS)(H_2O)_5]\cdot H_2O$ (**I**). In the crystal structure of **I** the Cu^{2+} ions are Jahn–Teller distorted and coordinated by six oxygen atoms (Figure 2). These belong to five molecules of water and one 1,3-benzenedisulfonic acid molecule. Four water molecules occupy the equatorial sites, whereas the sulfonate oxygen atom and one water molecule coordinate axially. Linkage to a 3D network occurs through hydrogen bonds (Figure 3).

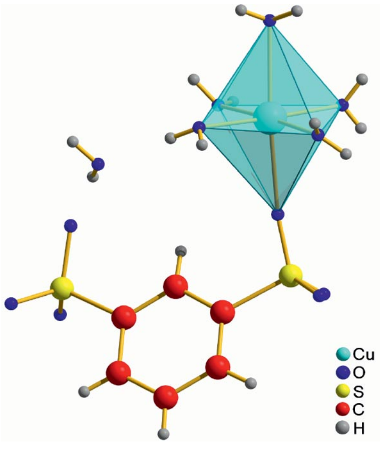


Figure 2. Typically distorted Cu^{2+} polyhedron shown for $[Cu(m\text{-}BDS)(H_2O)_5]\cdot H_2O$ (**I**).

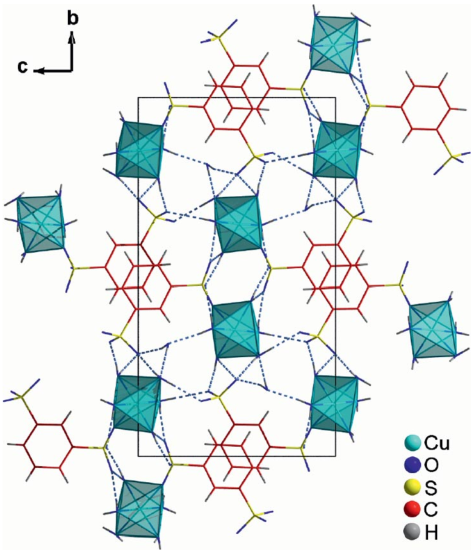


Figure 3. Projection of the crystal structure of $[Cu(m\text{-}BDS)(H_2O)_5]\cdot H_2O$ (**I**) onto the (100) plane. Hydrogen bonds are represented by dashed lines.

Copper *p*-Disulfonate

A direct link between the copper(II) ions is achieved, if the two sulfo groups are in *p*-positions. Blue single crystals of $[Cu(p\text{-}BDS)(H_2O)_4]$ (**II**) are obtained by conversion of 1,4-benzenedisulfonic acid **4** (*p*-$BDSH_2$) with $Cu_2(OH)_2(CO_3)$ in aqueous solution. The crystal structure shows distorted octahedral coordination (Jahn–Teller effect) of Cu^{2+} ions by four molecules of H_2O and two benzenedisulfonate ions. The linear organic linker connects the Cu^{2+} ions to form a chain by monodentate ligation of both sulfo functions. These chains form a 3D network by hydrogen bonding, which involves the free donor atoms of the sulfo groups (see Figures 4 and 5).

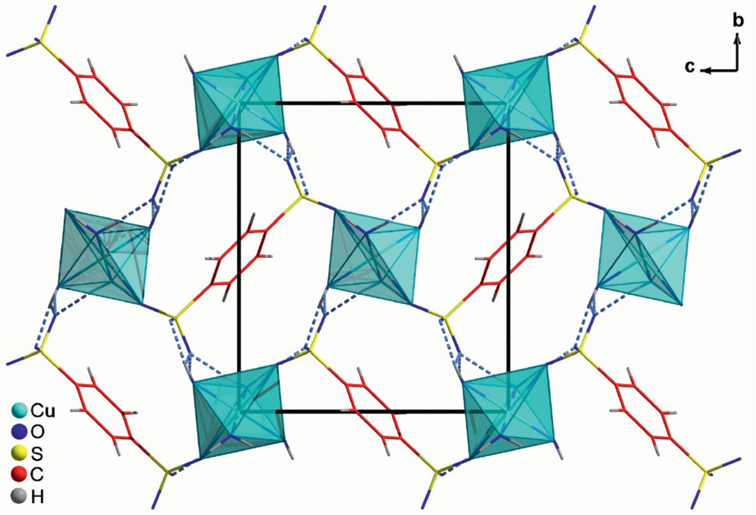


Figure 4. Connection of Cu^{2+} ions to form chains and formation of the network of [Cu(*p*-BDS)(H_2O)$_4$] (**II**) by hydrogen bonds (dashed lines) of the 1,4-benzene disulfonate linker.

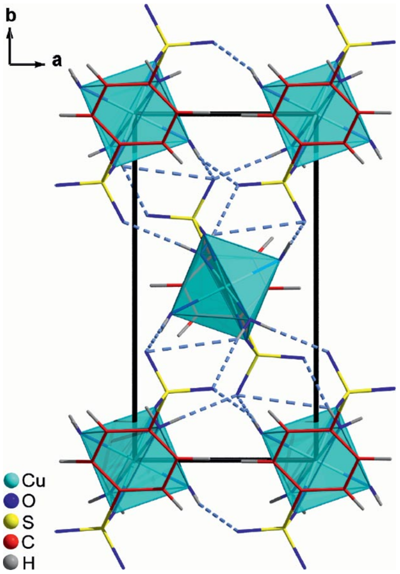


Figure 5. Projection of the crystal structure of [Cu(*p*-BDS)(H_2O)$_4$] (**II**) onto the (001) plane which shows the linkage of the chains to a 3D network through hydrogen bonds.

Copper Trisulfonate

Following the protocols for the synthesis of compounds **I** and **II**, [Cu_3(BTS)$_2$(H_2O)$_{12}$]·6H_2O (**III**) was prepared by conversion of benzenetrisulfonic acid (**5**) ($BTSH_3$) with $Cu_2(OH)_2(CO_3)$ in aqueous solution. Similar to the previous example, Cu^{2+} ions are coordinated by four molecules of water and two benzene trisulfonate ligands. The third sulfo function enlarges the coordination capacity and enables the linker to bind to two additional Cu^{2+} ions with formation of 2D layers (Figure 6 and 7). Superposition of the layers forms a network with channels along the *a* axis (Figure 8), in which noncoordinated water molecules are located. The network is formed by hydrogen bonding between the layers. The noncoordinated water molecules are also involved in these hydrogen bonds.

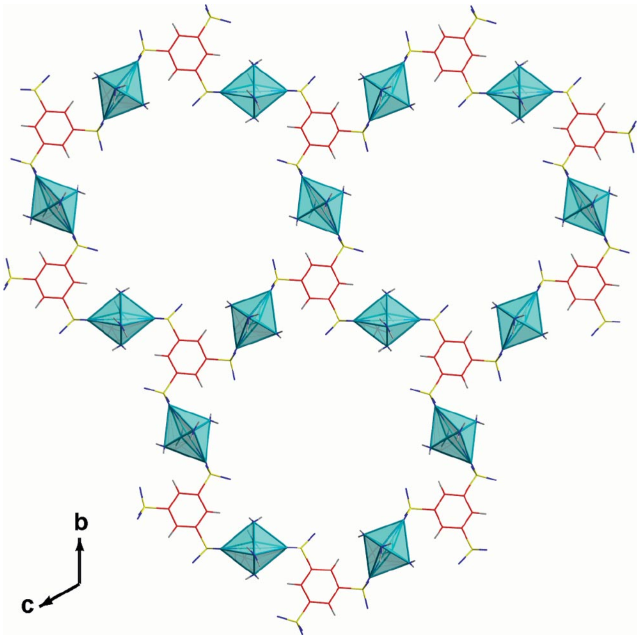


Figure 6. View onto a single layer of compound (**III**). Rotation (60°) and superposition of these layers generates the complete structure.

Thermal Analyses

The thermal decomposition of [Cu(*m*-BDS)(H_2O)$_5$]·H_2O (**I**), [Cu(*p*-BDS)(H_2O)$_4$] (**II**) and [Cu_3(BTS)$_2$(H_2O)$_{12}$]·6H_2O (**III**) has been studied by TG and DTA techniques under nitrogen flow. The degradation products of the anhydrous salts were identified by X-ray diffraction. The decomposi-

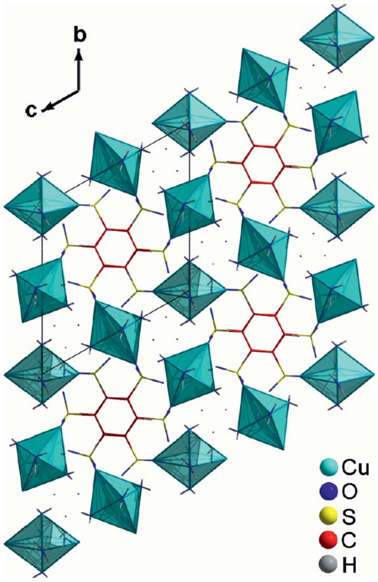


Figure 7. Projection of $[Cu_3(BTS)_2(H_2O)_{12}]\cdot 6H_2O$ (**III**) onto the (100)-plane.

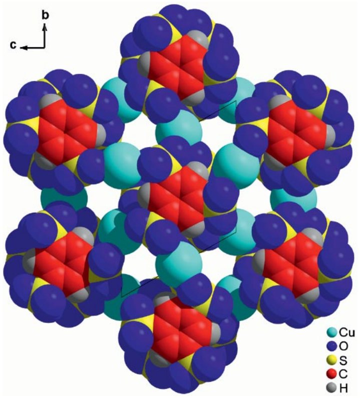


Figure 8. Space-filling representation of compound **III**, showing the open channels that permeate the solid down the *a* axis (solvent molecules are omitted).

tion of all samples occurs by two processes. The first stage is the dehydration of the compounds to their anhydrous forms, the second is the decomposition of these anhydrous compounds to a mixture of carbon and copper metal. The weight losses found during dehydration, as well as the calculated values, the number of water molecules lost in each case, and the temperature ranges are shown in Table 1.

The dehydration process of $[Cu(m\text{-}BDS)(H_2O)_5]\cdot H_2O$ (**I**) takes place in three successive steps corresponding to the loss of two water molecules in each step. The dehydrated salt is stable in a long temperature interval up to 340 °C and decomposes in the 340–420 °C temperature range with one endothermic effect shown in the DTA curve centered at 375 °C (Figure 9).

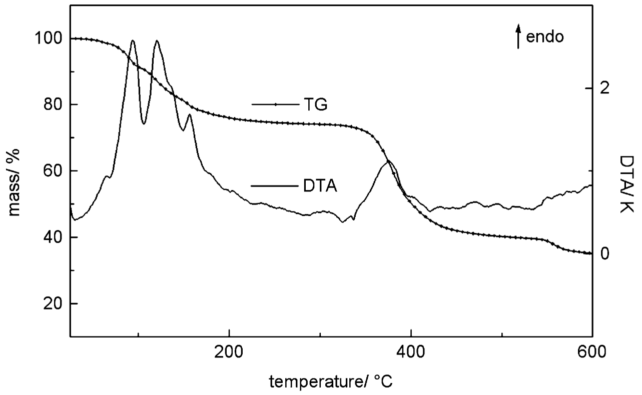


Figure 9. Thermal analysis of $[Cu(m\text{-}BDS)(H_2O)_5]\cdot H_2O$ (**I**).

The curves (TG and DTA) for $[Cu(p\text{-}BDS)(H_2O)_4]$ (**II**) show two thermogravimetric nondistinguishable steps corresponding to the loss of water starting at 120 °C. The observed mass loss is consistent with the calculation for four equivalents of H_2O (Figure 10). The anhydrous framework itself is stable. Its decomposition does not start below 400 °C and reaches a maximum at 430 °C. This value is about 200 K above the temperature observed for copper(II) terephthalate.[5]

For $[Cu_3(BTS)_2(H_2O)_{12}]\cdot 6H_2O$ (**III**) the dehydration process takes place in three successive steps (Figure 11). The first corresponds to the elimination of six solvent water molecules (presumably the noncoordinated ones in the channels along the *a* axis), the second and third to the loss of the twelve remaining water molecules. The anhydrous dehydrated framework itself is again stable up to 440 °C. The thermal decomposition of the framework proceeds above 440 °C.

Table 1. Data for thermal degradation.

Compound	Stage	T_{onset} [°C]	T_{end} [°C]	T_{max} [°C]	Mass loss obsd.	Mass loss calcd.
$[Cu(m\text{-}BDS)(H_2O)_5]\cdot H_2O$ (**I**)	1. loss of six equiv. of H_2O	70	210	90; 120; 155	25.7%	26.5%
	2. decomposition to Cu (calcd. 15.6%) and C	340	420	375	64.9%	–
$[Cu(p\text{-}BDS)(H_2O)_4]$ (**II**)	1. loss of four equiv. of H_2O	120	180	145; 170	19.4%	19.4%
	2. decomposition to Cu (calcd. 17.1%) and C	400	480	450	67.3%	–
$[Cu_3(BTS)_2(H_2O)_{12}]\cdot 6H_2O$ (**III**)	1. loss of 18 equiv. of H_2O	65	210	100; 125; 180	24.6%	28.9%
	2. decomposition to Cu (calcd. 17.0%) and C	440	470	455	73.8%	–

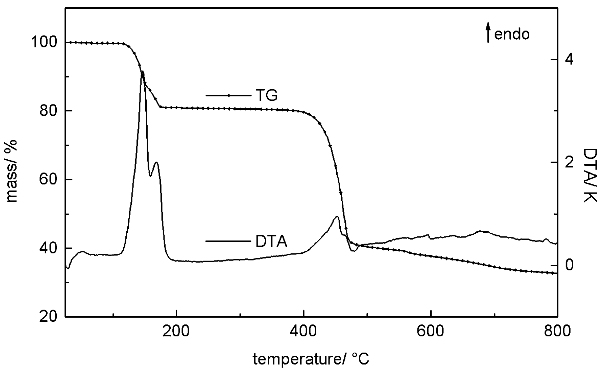


Figure 10. Thermal analysis of $[Cu(p\text{-}BDS)(H_2O)_4]$ (**II**).

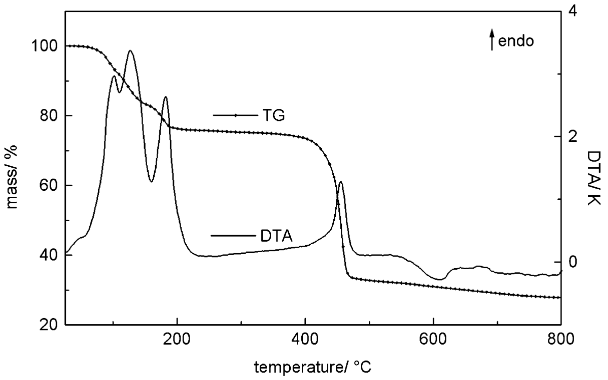


Figure 11. Thermal analysis of $[Cu_3(BTS)_2(H_2O)_{12}]\cdot 6H_2O$ (**III**).

Conclusions

A new route for synthesis of di- and trisulfonic acids was developed. 1,4-Benzenedisulfonate and 1,3,5-benzenetrisulfonate can be used as linkers for metal-organic frameworks. Their use in networks with copper(II) centers leads to a significant improvement of the thermal stability (with more than 400 °C) of the framework. Moreover, sulfonic acids exhibit clearly increased acidity ($pK_a \approx 0.7$) compared to the usually applied carboxylic acids ($pK_a \approx 4.2$). On the one hand, this feature overcomes synthetic limitations, since now weakly basic metal oxides or carbonates can be used as inorganic precursor compounds. On the other hand, chemical properties of the resulting frameworks could be different. MOFs with sulfonate linker units define therefore a new class of materials with unique and interesting properties. The significantly increased thermal stability is paramount. A condition for these new and promising materials is, however, the availability of sulfonic acids with suitable substitution patterns. The new two-step protocol for di- and trisulfonic acid synthesis from bromobenzene derivatives is a significant advance toward fulfilling this requirement. We will report on further sulfonic acid syntheses as well as novel framework structures derived from them in due course.

Experimental Section

General Methods: Preparative column chromatography was carried out using Merck SiO_2 (0.035–0.070 mm, type 60 A) with hexane and *tert*-butyl methyl ether (MTBE) as eluents. TLC was performed with Merck SiO_2 F_{254} plates on aluminum sheets. All starting materials were commercially available and were used without further purification. ^1H and ^{13}C NMR spectra were recorded with 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. A Thermo system equipped with AS 3000 autosampler and Finnigan MAT ESI-MS was used for LCMS. IR spectra were recorded with a Bruker Tensor 27 spectrometer equipped with a "GoldenGate" diamond ATR unit. Elemental analyses were measured with a Euro EA-CHNS from HEKAtech. Thermal analyses (TG and DTA) were performed with a Mettler-Toledo SDTA 851e. Data for X-ray single crystal structure determination were collected on a Bruker Apex II CCD diffractometer at 153(2) K with Mo-K_α radiation (graphite monochromator, λ = 71.07 pm). The structure was solved by direct methods and refined by full-matrix least-squares methods with SHELXL.

CCDC-738980 (for **I**), -738979 (for **II**) and -738978 (for **III**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1,4-Dimercaptobenzene (7): 1,4-Dibromobenzene (**6**) (2.4 g, 10 mmol, 1.0 equiv.) and NaS*i*Pr (4.7 g, 50 mmol, 5.0 equiv.) were suspended under an inert atmosphere (N_2) in dimethylacetamide (DMA) (30 mL) and the mixture was heated for 12 h to 100 °C. Subsequently, Na (1.6 g, 70 mmol, 7.0 equiv.) was added under vigorous stirring. In order to prevent foaming, more DMA (up to 5 mL) could be added. The resulting suspension was stirred for 16 h at 100 °C. If the conversion was incomplete (monitored by GLC), more Na (up to 1.6 g, 70 mmol, 7.0 equiv.) and (if necessary) DMA could be added and the mixture further stirred for 4–16 h at 100 °C. The mixture was carefully diluted with H_2O (250 mL) and *tert*-butyl methyl ether (MTBE) (150 mL) and acidified with concd. hydrochloric acid (pH < 1). The layers were separated and the aqueous layer extracted with MTBE (2 × 75 mL). The combined organic layers were washed twice with H_2O (2 × 100 mL) and dried ($MgSO_4$). After filtration, the solvent was evaporated and the crude product chromatographed twice [SiO_2, first with MTBE, then with hexane/MTBE, 5:1, R_f(hexane/MTBE, 10:1) = 0.20] to yield the title compound (1.3 g, 9.0 mmol, 90%) as a light yellow solid, m.p. 87 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.41 (s, 2 H, S-H), 7.16 (s, 4 H, 1-H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 127.94 (C-2), 130.36 (C-1) ppm. MS (EI, 70 eV): *m*/*z* (%) = 142 (100) [M^+], 109 (24), 97 (25), 78 (58), 69 (25). IR (ATR): $\tilde{\nu}$ = 3443 (w), 3069 (w), 2560 (m), 1899 (w), 1646 (w), 1477 (s), 1397 (m), 1263 (w), 1114 (s), 1013 (m), 906 (s), 812 (vs), 731 (s), 650 (w) cm^{-1}. $C_6H_6S_2$ (142.24 g/mol).

1,4-Benzenedisulfonic Acid Dihydrate (*p*-BDSH$_2$·2H$_2$O) (4): Dithiole **7** (1.3 g, 9.0 mmol, 1.0 equiv.) was dissolved with gentle warming in MeOH (18 mL) and H_2O_2 (30% in H_2O, 15.0 mL, 161 mmol, 17.7 equiv.) was added. The suspension was stirred for 16 h at 23 °C. Subsequently, all volatile materials were removed in high vacuum to yield the title compound (2.3 g, 8.4 mmol, 93%) as a colorless solid, mp. 83–84 °C. Thermal analysis (TG and DTA) showed this material to be the dihydrate, which is further confirmed by a single crystal structure analysis. ^1H NMR (CD_3OD, 500 MHz): δ = 5.44 (6 H, HDO), 7.90 (s, 4 H, 1-H) ppm. $^{13}C\{^1H\}$

NMR (CD_3OD, 125 MHz): δ = 127.04 (C-2), 147.92 (C-1) ppm. LC-MS (ESI, negative mode): *m*/*z* = 237 [M – H^+]. IR (ATR): $\tilde{\nu}$ = 3512–1504 [br, vs, ν(OH)], 3096 (w), 2561 (m), 2170 (m), 1809 (m), 1636 (m), 1395 (m), 1088 (vs), 1031 (vs), 990 (vs), 832 (s), 649 (vs) cm^{-1}. $C_6H_{10}S_2O_8$ (274.26 g/mol).

1,3,5-Trimercaptobenzene (9): 1,3,5-Tribromobenzene (**8**) (3.2 g, 10 mmol, 1.0 equiv.) and NaS*i*Pr (7.4 g, 75 mmol, 7.5 equiv.) were suspended under an inert atmosphere (N_2) in DMA (35 mL) and the mixture was heated for 12 h to 100 °C. Subsequently, Na (2.3 g, 100 mmol, 10 equiv.) was added under vigorous stirring. In order to prevent foaming, more DMA (up to 5 mL) could be added and the suspension was stirred for 16 h at 100 °C. More Na (2.3 g, 100 mmol, 10 equiv.) and (if necessary) DMA were added and the mixture was further stirred for 16 h at 100 °C. If the conversion was incomplete (monitored by GLC), more Na (up to 1.1 g, 50 mmol, 5.0 equiv.) and DMA (10 mL) were added and the mixture stirred for 4–16 h at 100 °C. The mixture was then carefully diluted with H_2O (250 mL) and MTBE (150 mL) and acidified with concd. hydrochloric acid (pH < 1). The layers were separated and the aqueous layer extracted with MTBE (2 × 75 mL). The combined organic layers were washed with H_2O (2 × 100 mL) and dried ($MgSO_4$). After filtration, the solvent was evaporated and the crude product chromatographed twice [SiO_2, first with MTBE, then with hexane/MTBE 5,:1, R_f(hexane/MTBE 10:1) = 0.35] to yield the title compound (1.3 g, 7.5 mmol, 75%) as a light yellow solid, mp. 57 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.41 (s, 3 H), 7.16 (s, 3 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 126.33 (CH), 132.98 (C) ppm. HR-MS (EI, 70 eV), calcd. for $C_6H_6S_3$: 173.9631; found 173.9632 [M^+]. IR (ATR): $\tilde{\nu}$ = 3461 (m), 2559 (s), 2533 (s), 1552 (vs), 1409 (s), 1370 (m), 1348 (m), 1293 (w), 1113 (s), 911 (m), 825 (s), 798 (s), 666 (s) cm^{-1}. $C_6H_6S_3$ (174.31 g/mol).

1,3,5-Benzenetrisulfonic Acid Trihydrate ($BTSH_3 \cdot 3H_2O$) (5): Trithiole **9** (1.3 g, 7.2 mmol, 1.0 equiv.) was dissolved with gentle warming in MeOH (15 mL) and H_2O_2 (30% in H_2O, 16.0 mL, 155 mmol, 21.5 equiv.) was added. The suspension was stirred for 16 h at 23 °C. Subsequently, all volatile materials were removed in high vacuum to yield the title compound (2.5 g, 6.8 mmol, 95%) as a colorless solid, mp. 123–124 °C. Thermal analysis (TG and DTA) showed this material to be the trihydrate. ^1H NMR (CD_3OD, 500 MHz): δ = 5.52 (9 H, HDO), 8.35 (s, 3 H, 2-H) ppm. $^{13}C\{^1H\}$ NMR (CD_3OD, 125 MHz): δ = 126.15 (CH), 146.92 (C) ppm. LC-MS (ESI, negative mode): *m*/*z* = 317 [M – H^+]. $C_6H_{12}S_3O_{12}$ (trihydrate, 372.35 g/mol).

Copper(II) (1,3-Benzenedisulfonate) Hexahydrate [Cu(*m*-BDS)-$(H_2O)_5$]·H_2O (I): Commercially available disodium *m*-benzenedisulfonate Na_2(*m*-BDS) was converted into the acid by ion exchange and the content of the aqueous solution was determined by titration with aqueous NaOH solution. [Cu(*m*-BDS)$(H_2O)_5$]·H_2O (**I**) was obtained by adding $Cu_2(OH)_2(CO_3)$ to an equimolar solution of 1,3-benzenedisulfonic acid in water at ambient temperature. The reaction mixture was stirred for 24 h at 50 °C and the pH-value was checked. If the reaction was incomplete (pH < 5), more $Cu_2(OH)_2(CO_3)$ was added. After filtration the blue solution was allowed to crystallize in air at room temperature. Blue, needle-shaped crystals were obtained after a few days.

Crystal Data for [Cu(*m*-BDS)$(H_2O)_5$]·H_2O (I): M_r = 407.85 g/mol, crystal size: 0.4 × 0.24 × 0.18 mm^3, monoclinic, $P2_1/n$, a = 632.05(4) pm, b = 2022.64(12) pm, c = 1128.30(8) pm, β = 99.263°(8), V = 1423.6(2) Å^3, Z = 4, 1.903 g/cm^3, μ = 18.86 cm^{-1}, 5.44° < 2θ < 5.18°, 13546 measured reflections, 2807 independent, R_{int} = 0.0375, R_1 = 0.0238, wR_2 = 0.0530, max./min. residual electron density: 0.411/–0.448.

Phase purity of the bulk material was proved by XRD at 23 °C. Lattice parameters were refined from the observed reflections as follows: a = 634.2(4) pm, b = 2020.2(12) pm, c = 1129.1(6) pm, β = 99.20°(4), V = 1427.9(14) Å^3.

Copper(II) (1,4-Benzenedisulfonate) Tetrahydrate [Cu(*p*-BDS)-$(H_2O)_4$] (II): A solution of $Cu_2(OH)_2(CO_3)$ (40 mg) and 1,4-benzenedisulfonic acid (0.1 g) in 5 mL water was heated at 50 °C whilst stirring for one day. If the reaction was incomplete (pH < 5), more $Cu_2(OH)_2(CO_3)$ was added. The resulting solution was filtered. After a few days in air at room temperature in a small petri dish blue crystals were obtained from the blue solution.

Crystal Data for [Cu(*p*-BDS)$(H_2O)_4$] (II): 371.82 g/mol, crystal size: 0.312 × 0.072 × 0.0674 mm^3, monoclinic, $P2_1/n$, a = 597.51(2) pm, b = 1093.60(3) pm, c = 992.16(3) pm, β = 105.165°(2), V = 625.74(3) Å^3, Z = 2, 1.973 g/cm^3, μ = 21.24 cm^{-1}, 7.24° < 2θ < 65.1°, 11842 measured reflections, 2267 independent, R_{int} = 0.0339, R_1 = 0.0237, wR_2 = 0.0583, max./min. residual electron density: 0.462/–0.351.

Phase purity of the bulk material was proved by XRD at 23 °C. Lattice parameters were refined from the observed reflections as follows: a = 598.8(3) pm, b = 1092.0(8) pm, c = 1000.0(5) pm, β = 105.12°(4), V = 631.3(3) Å^3.

Tricopper(II) Bis(1,3,5-benzenetrisulfonate) Octadecahydrate [Cu_3-$(BTS)_2(H_2O)_{12}$]·6 H_2O (III): To an aqueous solution of 1,3,5-benzenetrisulfonic acid (0.1 g in 10 mL water) $Cu_2(OH)_2(CO_3)$ (45.5 mg) was added under vigorous stirring. The reaction mixture was heated to 50 °C for one day. If the reaction was incomplete (pH < 5), more $Cu_2(OH)_2(CO_3)$ was added. the blue solution was allowed to crystallize in air at room temperature. Blue plate-shaped crystals were obtained after a few days.

Crystal Data for [$Cu_3(BTS)_2(H_2O)_{12}$]·6 H_2O (III): 1145.44 g/mol, crystal size: 0.313 × 0.204 × 0.089 mm^3, triclinic, $P\bar{1}$, a = 815.45(4) pm, b = 1146.06(9) pm, c = 1146.97(6) pm, α = 114.593°(3), β = 102.453°(2), γ = 103.841°(3), V = 884.00(9) Å^3, Z = 1, 1.973 g/cm^3, μ = 22.70 cm^{-1}, 7.00° < 2θ < 72.26°, 31444 measured reflections, 8322 independent, R_{int} = 0.0355, R_1 = 0.0877, wR_2 = 0.1612, max./min. residual electron density: 1.313/–1.579.

Phase purity of the bulk material was proved by XRD at 23 °C. Lattice parameters were refined from the observed reflections as follows: a = 817.7(2) pm, b = 1151.8(4) pm, c = 1150.9(5) pm, α = 114.59°(6), β = 103.51°(7), γ = 103.69°(3), V = 887.4(8) Å^3.

Acknowledgments

We are grateful to Christina Zitzer and Willi Rathje for initial experiments on this project and to Wolfgang Saak and Detlev Haase for help with the single-crystal X-ray analysis.

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Received: September 14, 2009