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# *trans*-1,2-Cyclohexanedisulfonic Acid: An Optically Active Linker for Coordination Polymers

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Dedicated to Professor Rüdiger Beckhaus on the occasion of his 60th birthday

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Racemic 1,2-cyclohexanedisulfonic acid was prepared from cyclohexene oxide via the cyclic trithiocarbonate and isolated as its barium salt. Optical resolution was achieved by crystallization with (-)-(R,R)-1,2-cyclohexane diamine; the absolute configuration was established by X-ray crystallography of this salt,  $[C_6H_{10}(NH_3)_2][C_6H_{10}(SO_3)_2]$ . Solid-state structures were investigated of the racemic acidic sodium disulfonate  $Na(H_5O_2)[C_6H_{10}(SO_3)_2]$  and the optically active disulfonates  $Na_2[C_6H_{10}(SO_3)_2]\cdot 1.8H_2O$  and  $Ag(NH_2Me_2)\cdot [C_6H_{10}(SO_3)_2]$ .

# Introduction

Metal-organic frameworks (MOFs) are an emerging class of materials with several highly promising properties. Flourishing fields in which they are found are catalysis<sup>[1]</sup> and renewable energies (in particular, gas-storage<sup>[2]</sup> and separation<sup>[3]</sup> technologies as well as fuel-cell applications).<sup>[4]</sup> With regard to the organic linker molecules, di- and oligocarboxylic acids form the foundation of the synthesis of MOFs.<sup>[5]</sup> To expand the structural diversity of this compound class and other coordination polymers, we have initiated research on the preparation of new di- and oligosulfonic acids,<sup>[6]</sup> which possess promising and advantageous properties compared to carboxylic acids, such as stronger acidity and enhanced thermal stability. Apart from aromatic sulfonic acids, we have so far prepared two aliphatic disulfonic acids with a conformationally rigid backbone: trans-1,4-cyclohexanedisulfonic acid (1)<sup>[7]</sup> and octahydropentalene-2,5-disulfonic acid  $(2)^{[8]}$  as single diastereoisomers, which are both achiral compounds (Figure 1). To ac-



Figure 1. Aliphatic disulfonic acids.

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cess chiral, enantiomerically pure frameworks, we wish to report now on the synthesis of an optically active, aliphatic disulfonic acid **3**. The respective congener *trans*-1,2-cyclo-hexanedicarboxylic acid has been reported as a linker molecule for coordination polymers.<sup>[9]</sup>

#### **Results and Discussion**

After some experimentation with activation and nucleophilic displacement reactions of trans-1,2-cyclohexanediol, we considered trithiocarbonate 5 as the most convenient starting material for racemic disulfonic acid 3 (Scheme 1).<sup>[10]</sup> Intermediate product 5 is prepared from cyclohexene oxide and CS<sub>2</sub>, as was reported several times in the literature, although spectroscopic characterization of compound 5 was so far not sufficient.<sup>[11]</sup> Its relative configuration was established to be trans by X-ray crystallography.<sup>[12]</sup> Compound 5 was oxidized with an excess amount of H<sub>2</sub>O<sub>2</sub>, which resulted in a reaction mixture containing the racemic acid  $(\pm)$ -3. The latter was precipitated as its barium salt ( $\pm$ )-6 together with BaSO<sub>4</sub>, and extracted from the precipitate with hot water and recrystallized as the barium salt  $(\pm)$ -6.

An aqueous solution of a small sample of barium salt  $(\pm)$ -6 was protonated by a column of ion-exchange resin Amberlyst 15 and the free acid  $(\pm)$ -3 was neutralized with NaHCO<sub>3</sub>. After slow evaporation of water, the racemic mono-sodium salt  $(\pm)$ -7 was obtained as crystalline material suitable for X-ray single-crystal structure analysis (Table 1, see the Exp. Sect.), which confirmed the relative *trans* configuration (Figure 2). Compound  $(\pm)$ -7 crystallized as a racemate, that is, it contained both enantiomers





Scheme 1. Synthesis of the racemic barium salt ( $\pm$ )-6. Reagents and conditions: (a) CS<sub>2</sub> (3.0 equiv.), KOH (2.5 equiv.), MeOH, 23 °C, 4 h; (b) 1. H<sub>2</sub>O<sub>2</sub> (20 equiv.; 30% in H<sub>2</sub>O), AcOH, 23 °C, 20 h; 2. BaCl<sub>2</sub>·2H<sub>2</sub>O (1.9 equiv.).

of the disulfonate anion (R, R and S, S configuration) in the unit cell. The structure is completed by a Na<sup>+</sup> ion and the so-called Zundel ion,  $H_5O_2^+$  (Figure 2).<sup>[13]</sup> The disulfonate anions are arranged in a way that their [SO<sub>3</sub>] moieties and the two different cations form an "inorganic" layer, whereas the cyclohexane rings of the anions form an "organic" layer. The cyclohexane rings are in a chair conformation with C-C single-bond lengths between 151.9(2) and 154.3(1) pm, as expected. The longest bond was found between the carbon atoms (C1) that are connected to the [SO<sub>3</sub>] groups. The distance S1-C1 is 180.74(7) pm, whereas the S-O bonds are found uniformly at about 146 pm. This is slightly larger than that expected for a typical S-O double bond (142-143 pm) and can be attributed to the coordination of the oxygen atom by the cations. Atoms O2 and O3 are attached to Na<sup>+</sup> ions, what results in slightly distorted [NaO<sub>6</sub>] octa-



Figure 2. Crystal structure of the racemic monosodium salt  $Na(H_5O_2)[C_6H_{10}(SO_3)_2]$  [(±)-7] as a projection onto the (001) plane. The configuration of the crystallographically equivalent anions is indicated (*R* and *S*, respectively). The hydrogen bond within the  $H_5O_2^+$  ion is emphasized as a black line. Note that the hydrogen atom within this bond is split on two positions, a typical double-minimum situation that is often observed for strong hydrogen bonds are shown as dashed lines. Important distances [pm]: S1–O1 145.98(6), S1–O2 146.88(5), S1–O3 145.87(6), S1–C1 180.74(7), Na1–O2 235.22(6) (2×), Na1–O3 233.62(5) (2×), Na1–O3 235.80(6) (2×), O4–O4 241.9(1), O4–O1 268.90(9), O4–O2 273.56(9).

hedra displaying distances Na-O of around 235 pm. Oxygen atom O1 is strongly involved in a hydrogen bond to the H<sub>5</sub>O<sub>2</sub><sup>+</sup> ion. According to the distance O1-O4 of 268.90(9) pm, this hydrogen bond is quite strong.<sup>[14]</sup> This assumption is supported by an angle of  $165(2)^{\circ}$  for  $\angle(O4-$ H4a–O1), which is near to linearity. The oxygen atom O2 takes part not only in Na<sup>+</sup> coordination, but shows also a strong hydrogen bridge to the Zundel ion. The respective distance O4–O2 and the angle  $\angle$ (O4–H4b–O2) are 273.56(9) pm and 167(2)°, respectively. The strongest hydrogen bond, however, is found within the  $H_5O_2^+$  ion. The distance between the two symmetry-related oxygen atoms O4 is short [241.9(1) pm]. By means of X-ray diffraction it cannot be decided whether the hydrogen bond is symmetric. With respect to difference Fourier maps it seems that the atom is distributed on two crystallographic sites according to the double-minimum potential situation often found for such short hydrogen bonds.<sup>[13–15]</sup> It is interesting to see that the  $H_5O_2^+$  ions are located in channels along the [001] direction that are formed due to the specific arrangement of the disulfonate anions. With respect to this structural feature and the observed hydrogen-bonding system, it is quite likely that anisotropic protonic conduction might occur along the channels.

Resolution of racemic sulfonic acids or amines as the ammonium salt with either optically active acid or amine is an established concept for the synthesis of enantiopure materials.<sup>[16,17]</sup> For compound 3, the racemic barium salt  $(\pm)$ -6 was protonated with a column of ion-exchange resin Amberlyst 15 and the aqueous solution was treated with a little less than half an equivalent of (-)-(R,R)-1,2-diaminocyclohexane (Scheme 2).<sup>[18]</sup> The resulting diammonium salt (+)-8 was repeatedly recrystallized from MeOH until the optical rotation was constant. The supernatant solutions were combined, and enantiomer (-)-8 was obtained by crystallization with (+)-(S,S)-1,2-diaminocyclohexane. Gratifyingly, compound (+)-8 gave single crystals suitable for X-ray crystallography (Figure 3). Thus, with known configuration of the amine the absolute configuration of the sulfonate could be established to be S,S. Again, the free acids (+)-(S,S)-3 and (-)-(R,R)-3 were obtained by protonation with Amberlyst 15 and evaporation of water as the dihydrate.



Scheme 2. Resolution of *trans*-cyclohexanedisulfonic acid; the title compound (+)-3 is obtained as the dihydrate. Reagents and conditions: (a) 1. protonation with Amberlyst 15; 2. (-)-(R,R)-1,2-cyclohexanediamine (0.4 equiv.); (b) protonation with Amberlyst 15.

The crystal structure of  $[C_6H_{10}(NH_3)_2][C_6H_{10}(SO_3)_2]$ [(+)-8] is of particular interest, not only because this ammonium salt was used for the separation of the enantiomers, but also because it is the first example of a disulfonate that is crystallized by using a cation that has the same organic scaffold as the anion. The compound crystallized orthorhombically with the noncentrosymmetric space group



Figure 3. Crystal structure of the optically active salt of  $[C_6H_{10}(NH_3)_2][C_6H_{10}(SO_3)_2]$  [(+)-8] as a projection onto the (100) plane (on top) and the hydrogen-bonding system between cations and anions (at the bottom). The lower part of the figure shows the strand emphasized in the upper part (light blue circle) turned by 90°. The absolute configuration of the building blocks is indicated by *R* and *S*. Important distances [pm]: S1–O1 146.0(2), S1–O2 145.9(2), S1–O3 144.8(2), S1–C1 181.3(2), S2–O4 145.8(2), S2–O5 145.7(2), S2–O6 145.7(2), S2–C6 182.0(2), N1–O5 288.9(2), N1–O6 291.0(2), N1–O4 284.2(2), N1–O2 291.5(2), N2–O2 276.4(2), N2–O1 278.5(2), N2–O3 282.5(2), N2–O5 280.2(2).

 $P2_12_12_1$ . Crystallographically there is one diammonium cation,  $[C_6H_{10}(NH_3)_2]^{2+}$  and one disulfonate anion  $[C_6H_{10}(SO_3)_2]^{2-}$  in the structure. The cation shows *R*,*R* configuration whereas the anion is the *S*,*S* enantiomer (Figure 3, on top). In both the anion and cation the cyclohex-

ane moieties have essentially the same C-C bond lengths. In the cation, however, the typical bond elongation that is observed in the anion for the sulfur-bonded carbon atoms  $(C-C \approx 155 \text{ pm})$  cannot be seen. The distances N1–C7 and N2-C8 are 150.0(3) and 149.6(3) pm, respectively, in line with the expectations for an N-C single bond. The S-O bond lengths in the anion are 181.3(2) (C1-S1) and 182.0(2) pm (C6–S2) in accordance with the findings for the compound described above. In the crystal structure the cations and anions are arranged in a way that the [NH<sub>3</sub>] and [SO<sub>3</sub>] moieties are forming one layer and the cyclohexane rings a second one (Figure 3). This situation is very similar to the findings for  $Na(H_5O_2)[C_6H_{10}(SO_3)_2][(\pm)-7]$ . The assembling of the building blocks is certainly driven by the occurrence of hydrogen bonds. These exist between the nitrogen atoms as donors and the oxygen atoms of the [SO<sub>3</sub>] groups as acceptors. The hydrogen bonds lead to the formation of strands running along the [100] direction of the unit cell (Figure 3, at bottom). Thus, the hydrogen bonds do not occur pairwise between cation and anion but each [NH<sub>3</sub>] has two [SO<sub>3</sub>] groups as acceptors and vice versa. This is achieved by a quite complicated system of bifurcated hydrogen bonds. As is typical for such types of hydrogen bridges, the donor-acceptor distances are significantly larger than those expected for strong hydrogen bonds and the angles  $\angle$  (D–H–A) deviate strongly from linearity.<sup>[14]</sup> In the present case distances N-O between 276.4(2) and 291.5(2) pm are found and the respective angles range from 94(1) up to 154(1)°.

After neutralization of acid (-)-(R,R)-3 with NaHCO<sub>3</sub>, single crystals of the optically active disodium salt Na<sub>2</sub>[C<sub>6</sub>H<sub>10</sub>(SO<sub>3</sub>)<sub>2</sub>]·1.8H<sub>2</sub>O [(R,R)-9] were obtained, which were submitted to X-ray structure analysis (Figure 4). Furthermore, when heating acid (+)-(S,S)-3 up to 105 °C with Ag<sub>2</sub>CO<sub>3</sub> in dimethylformamide (DMF) in a sealed tube, single crystals of a mixed silver(I) dimethylammonium salt (R,R)-10 were obtained and investigated by X-ray crystallography (Figure 5). The dimethylamine is presumably formed from the solvent DMF under the reaction conditions.



Figure 4. Crystal structure of the optically active disodium salt  $Na_2[C_6H_{10}S_2O_6]$ ·1.8H<sub>2</sub>O [(*R*,*R*)-9] as a projection onto the (100) plane. The cyclohexane rings of the disulfonate anions are arranged into circles (emphasized by light blue ellipsoids) that are surrounded by Na<sup>+</sup> ions. These are connected by the [SO<sub>3</sub>] moieties of the disulfonate groups and further coordinated by H<sub>2</sub>O molecules (shown in turquoise). Important distance ranges [pm]: S–O 145.3(2)–147.0(2), S–C 179.4(2)–182.2(2), Na–O 227.3(2)–294.4(2).



Figure 5. Perspective view of the crystal structure of  $Ag(NH_2Me_2)[C_6H_{10}(SO_3)_2]$  [(*R*,*R*)-**10**] along the [010] direction (on top). In this direction anionic chains  $[AgC_6H_{10}(SO_3)_2]^-$  are running, which are depicted in more detail in the lower part of the figure. The Ag<sup>+</sup> ions are in a distorted-octahedral coordination of oxygen atoms that originate from three disulfonate anions. Important distances [pm]: Ag1–O11 243.4(2), Ag1–O12 244.7(2), Ag1–O12 286.7(2), Ag1–O14 242.9(2), Ag1–O14 257.6(2), Ag1–O16 233.9(2), S1–O11 147.0(2), S1–O12 146.3(2), S1–O13 145.8(2), S1–C1 180.7(2), S2–O14 146.4(2), S2–O15 145.7(2), S2–O16 146.4(2), S2–C2 180.6(2), C1–C2 154.2(3).

The sodium compound (R,R)-9 crystallized with triclinic symmetry and must be described in the noncentrosymmetric space group P1 (Figure 4). The number of formula units is 5, so that crystallographically ten Na<sup>+</sup> ions, five disulfonate anions, and nine H<sub>2</sub>O molecules are present in the unit cell. Similarly to the structure of  $(\pm)$ -7, there is quite a clear separation between the organic and inorganic moieties of the structure. However, in contrast to the racemic sodium compound, which shows the different parts of the structure arranged into layers, in compound (R,R)-9 five of the cyclohexane chairs are arranged in a ring that is surrounded by Na<sup>+</sup> ions and water molecules. The five disulfonate anions show essentially the same structural characteristics as observed in  $(\pm)$ -7. Thus, the C–C bond lengths within the cyclohexane ring are slightly larger for those carbon atoms that are bonded to the  $[SO_3]$  groups [154.4(2)-155.2(2) pm]. The distances S–C lie in the narrow range from 179.4(2) up to 181.2(2) pm. Within the [SO<sub>3</sub>] moieties of the anions the distances S-O are found between

145.3(2) and 147.0(2) pm. The shortest distances belong to oxygen atoms that do not coordinate to Na<sup>+</sup> ions. However, most of them are part of the coordination sphere of the ten Na<sup>+</sup> ions. Most of the sodium atoms are in six- or sevenfold coordination of oxygen atoms; only atom Na9 has a coordination number of five if distances up to 320 pm are taken into account. For most of the sodium ions H<sub>2</sub>O molecules act as further ligands, and only Na3 and Na7 are solely coordinated by [SO<sub>3</sub>] groups. The number of H<sub>2</sub>O molecules within the [NaO<sub>n</sub>] polyhedra is either three (Na1, Na5, Na6), two (Na2, Na4), or one (Na8, Na9, Na10). The H<sub>2</sub>O molecules take part in a complex hydrogen-bonding system and these bonds can be classified as medium strong with respect to the donor–acceptor distances, which range from 2.783(2) to 2.957(2) pm.

The silver compound  $Ag(NH_2Me_2)[C_6H_{10}(SO_3)_2][(R,R)-$ 10] crystallized in the noncentrosymmetric space group  $P2_1$ and contained the R,R enantiomer of the cyclohexanedisulfonate anion. The structure of the compound is stamped by anionic chains according to  ${}^{1}_{\infty}{Ag[C_{6}H_{10}(SO_{3})_{2}]_{3/3}}^{-1}$ (Figure 5, lower part). In this chain each Ag<sup>+</sup> ion is coordinated by three chelating anions, which involve both  $[SO_3]$ moieties of the disulfonate groups. Each anion is coordinated further to two silver ions. Five of the six distances Ag–O are lying in the range between 233.9(2) and 257.6 pm; the sixth one is significantly longer [Ag1–O12 286.7(2) pm]. The strong linkage of the Ag<sup>+</sup> ions leads to quite short distances Ag-Ag of only 305.8(2) pm. The structural parameters of the cyclodisulfonate anion are in line with the findings for the compounds described so far. Thus, the distances S–O within the [SO<sub>3</sub>] groups fall in a narrow range between 145.7(2) and 146.4(2) pm and the bond lengths S-C are 180.7(2) and 180.6(2) pm, respectively. The anionic chains are arranged into layers that expand in the (100) plane. The charge-compensating dimethylammonium ions are located between these layers . These cations originate from decomposition of the DMF solvent.

### **Experimental Section**

**General:** <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker Avance ARX 300 and DRX 500 instruments at 23 °C in CDCl<sub>3</sub>. Multiplicities of carbon signals were determined with distortionless enhancement by polarization transfer (DEPT) experiments. MS and HRMS spectra were obtained with a Finnigan MAT95 (EI) and a Waters Q-TOF Premier (ESI) spectrometer. IR spectra were recorded on a Bruker Tensor 27 spectrometer equipped with a "GoldenGate" diamond attenuated total reflection (ATR) unit. Elemental analyses were measured with a Euro EA-CHNS instrument from HEKAtech. A column of ion-exchange resin Amberlyst 15 (Fluka) was used with capacity 12 mmolg<sup>-1</sup>. This column was regenerated with concentrated hydrochloric acid (100 mL) after each preparation and reused.

X-ray Crystallography: The single crystals obtained were transferred into inert oil for protection (AB128333, ABCR, Karlsruhe, Germany). Under a cooling nitrogen stream, suitable crystals were mounted onto glass needles ( $\emptyset = 0.1 \text{ mm}$ ) and immediately placed into a stream of cold N<sub>2</sub> (–120 °C) inside the diffractometer ( $\kappa$ -APEX II, Bruker, Karlsruhe, Germany). After unit-cell determi-



Table 1. Crystal data and structure refinement for	compounds $(\pm)$ -7, $(+)$ -8, $(-)$ - $(R,R)$ -9, and $(R,R)$ -10
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	(±) <b>-7</b>	(+)-8	(-)-( <i>R</i> , <i>R</i> )-9	(R,R)-10
Empirical formula	C <sub>6</sub> H <sub>15</sub> NaO <sub>8</sub> S <sub>2</sub>	$C_{12}H_{26}N_2O_6S_2$	C <sub>30</sub> H <sub>68</sub> Na <sub>10</sub> O <sub>39</sub> S <sub>10</sub>	C <sub>8</sub> H <sub>18</sub> AgNO <sub>6</sub> S <sub>2</sub>
Formula weight	302.29	358.47	1603.34	396.22
Temperature [K]	120(2)	120(2)	100(2)	100
Wavelength [pm]	71.073	71.073	71.073	71.073
Crystal system	monoclinic	orthorhombic	triclinic	monoclinic
Space group	C2/c	$P2_{1}2_{1}2_{1}$	<i>P</i> 1	$P2_1$
a [pm]	a = 990.70(3)	a = 548.45(4)	a = 585.25(2)	a = 915.60(3)
<i>b</i> [pm]	b = 2267.51(7)	b = 1160.62(8)	b = 1608.00(5)	b = 544.51(2)
<i>c</i> [pm]	c = 536.43(2)	c = 2496.48(18)	c = 1749.71(5)	c = 1356.38(4)
a [°]	_	_	69.5738(14)	_
β[°]	94.3470(10)	_	81.3982(14)	100.049(2)
γ [°]	_	_	81.0585(14)	_
Volume [10 <sup>6</sup> pm <sup>3</sup> ]	1201.58(7)	1589.1(2)	1516.17(8)	665.85(4)
Ζ	4	4	1	2
Density (calcd.) [Mgm <sup>-3</sup> ]	1.671	1.498	1.756	1.976
Absorption coefficient [mm <sup>-1</sup> ]	0.505	0.366	0.537	1.845
F(000)	632	768	830	400.0
Crystal size [mm <sup>3</sup> ]	$0.24 \times 0.07 \times 0.05$	$0.31 \times 0.19 \times 0.05$	$0.34 \times 0.08 \times 0.04$	$0.212 \times 0.123 \times 0.05$
$\theta$ range for data collection [°]	1.80 to 36.32	3.01 to 29.74	1.25 to 33.73	1.53 to 30.09
Index ranges	$-16 \le h \le 16$	$-7 \le h \le 7$	$-9 \le h \le 9$	$-12 \le h \le 12$
-	$-37 \le k \le 37$	$-16 \le k \le 16$	$-25 \le k \le 25$	$-7 \le k \le 7$
	$-8 \le l \le 8$	$-34 \leq l \leq 34$	$-27 \le l \le 27$	$-19 \le l \le 19$
Reflections collected	34188	46033	155402	20907
Independent reflections	2915 ( $R_{\rm int} = 0.0350$ )	$4522 (R_{int} = 0.0751)$	$24234 \ (R_{\rm int} = 0.0373)$	$3912 (R_{int} = 0.0252)$
Completeness [%]	100	99.8	100	100
Absorption correction	multiscan	numerical	multiscan	numerical
Max. and min. transmission	0.975 and 0.888	0.9805 and 0.8951	0.979 and 0.839	0.913 and 0.696
Data/restraints/parameters	2915/0/90	4522/0/201	24234/21/856	3912/1/165
Goodness-of-fit on $F^2$	1.130	1.084	1.040	1.074
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0229,$	$R_1 = 0.0405,$	$R_1 = 0.0248,$	$R_1 = 0.0154,$
	$wR_2 = 0.0602$	$wR_2 = 0.0848$	$wR_2 = 0.0542$	$wR_2 = 0.0371$
R indices (all data)	$R_1 = 0.0293,$	$R_1 = 0.0501,$	$R_1 = 0.0292,$	$R_1 = 0.0165,$
	$wR_2 = 0.0634$	$wR_2 = 0.0886$	$wR_2 = 0.0557$	$wR_2 = 0.0375$
Flack-X	-	0.01(7)	0.022(8)	0.008(8)
Largest diff. peak and hole $[e Å^{-3}]$	0.622 and -0.308	0.318 and -0.576	0.554 and -0.462	0.41 and -0.28

nation, reflection intensities of the respective best specimens were collected. The structure solutions were successful by using direct methods and full-matrix least-squares refinements on  $|F^2|$  were performed, introducing anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located in difference Fourier maps. Those bonded to carbon atoms were in each case refined in fixed positions ("riding model"). Oxygen-bonded hydrogen atoms were freely refined, except for Na<sub>2</sub>[C<sub>6</sub>H<sub>10</sub>(SO<sub>3</sub>)<sub>2</sub>]-1.8H<sub>2</sub>O. Structure solution and refinement were performed with the SHELX system.<sup>[19]</sup> Table 1 shows a summary of the X-ray crystallography data.

CCDC-1016222 [( $\pm$ )-7], -1016224 [(+)-8], -1016225 [(–)-(*R*,*R*)-9], and -1025601 [(*R*,*R*)-10] 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.

(±)-*trans*-Hexahydro-1,3-benzodithiole-2-thione (5): Cyclohexene oxide (4) (5.0 mL, 49 mmol) was added to a solution of carbon disulfide (9.0 mL, 150 mmol) and potassium hydroxide (6.9 g, 0.12 mol) in methanol (30 mL) at 0 °C. After warming to ambient temperature, the reaction mixture was stirred for 4 h. After addition of water (100 mL), methanol and the excess amount of carbon disulfide were evaporated under vacuum. The precipitate was removed by filtration, washed with water ( $2 \times 30$  mL), and dried under vacuum to yield the title compound (8.64 g, 45.4 mmol, 92%) as a yellow solid, m.p. 164 °C (ref.<sup>[11a]</sup> 164–165 °C). <sup>1</sup>H NMR

(500 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.18–4.00 (m, 2 H), 2.23–2.16 (m, 2 H), 2.02–1.89 (m, 2 H), 1.79–1.65 (m, 2 H), 1.52–1.40 (m, 2 H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  = 226.91 (C), 64.47 (2 CH), 29.07 (2 CH<sub>2</sub>), 25.04 (2 CH<sub>2</sub>) ppm. IR (ATR):  $\tilde{v}$  = 2937 (m), 2854 (m), 1440 (m), 1329 (w), 1279 (m), 1223 (w), 1195 (w), 1100 (m), 1057 (s), 1033 (s), 1014 (m), 988 (m), 907 (w), 863 (s), 840 (m), 817 (m), 743 (m) cm<sup>-1</sup>. MS (EI, 70 eV): *mlz* (%): 190 (100) [M<sup>+</sup>], 81 (70), 73 (30). HRMS (EI, 70 eV): calcd. for C<sub>7</sub>H<sub>10</sub>S<sub>3</sub> 189.9945; found 189.9940 [M<sup>+</sup>]. C<sub>7</sub>H<sub>10</sub>S<sub>3</sub> (190.35): calcd. C 44.17, H 5.30, S 50.53; found C 44.19, H 5.33, S 50.57.

(±)-Barium trans-1,2-Cyclohexanedisulfonate [(±)-6]: Hydrogen peroxide (30% solution in water, 10.7 mL, 105 mmol) was added to a suspension of trithiocarbonate 5 (1.00 g, 5.25 mmol) in acetic acid (25 mL). The resulting mixture was stirred at ambient temperature until the yellow color fully disappeared (about 20 h). A solution of BaCl<sub>2</sub>·2H<sub>2</sub>O (2.49 g, 10.2 mmol) in water (25 mL) was added forming a suspension. The volatiles were completely removed under reduced pressure. The residue was suspended in hot water (200 mL), filtered, and the filtrate evaporated again. The resulting solid was washed with hot ethanol (100 mL) and dried under high vacuum to give the product (1.45 g, 3.83 mmol, 73%) as a colorless solid, m.p. >400 °C. <sup>1</sup>H NMR (500 MHz,  $D_2O$ ):  $\delta$  = 3.68-3.63 (m, 2 H), 2.30-2.23 (m, 2 H), 2.23-2.10 (m, 2 H), 1.87-1.75 (m, 2 H), 1.73–1.55 (m, 2 H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz,  $D_2O$ ):  $\delta$  = 55.01 (CH), 21.98 (CH<sub>2</sub>), 19.56 (CH<sub>2</sub>) ppm. IR (ATR):  $\tilde{v} = 3534$  (w), 3433 (w), 3127 (br), 2945 (w), 2862 (w), 1671 (w),



1639 (w), 1453 (w), 1222 (m), 1162 (s), 1062 (m), 1040 (m), 987 (w), 823 (w), 776 (m), 767 (m), 647 (m), 625 (m), 554 (m), 540 (m) cm<sup>-1</sup>.  $C_6H_{10}BaO_6S_2$  (379.59): calcd. C 18.99, H 2.66, S 16.89; found C 18.92, H 2.69, S 16.87.

(±)-trans-1,2-Cyclohexanedisulfonic Acid Monosodium Salt Dihydrate [(±)-7]: Barium salt (±)-6 (75 mg, 198 µmol) was suspended in water (5 mL) and transferred on top of a column (20 g, Amberlyst 15). The corresponding acid was eluted with water until the pH of the eluent was neutral (ca. 30 mL). The resulting solution was concentrated under vacuum, redissolved in water (5 mL), and treated with NaHCO<sub>3</sub> (32 mg, 386 µmol). Slow evaporation of the solvent at ambient temperature yielded the title compound (±)-7 as colorless crystals (59 mg, 194 µmol, 98%) suitable for X-ray analysis. C<sub>6</sub>H<sub>15</sub>NaO<sub>8</sub>S<sub>2</sub> (302.29): calcd. C 23.84, H 5.00, S 21.21; found C 24.01, H 4.98, S 20.96.

(R,R)-1,2-Cyclohexanediammonium (S,S)-1,2-Cyclohexanedisulfonate [(+)-8] and Its Enantiomer (-)-8: Barium salt  $(\pm)-6$  (1.80 g, 4.74 mmol) was suspended in water (50 mL) and transferred on top of a column (20 g, Amberlyst 15). The corresponding acid was eluted with water until the pH of the eluent was neutral (ca. 150 mL). The resulting solution was treated with (R,R)-1,2-diaminocyclohexane (217 mg, 1.90 mmol) and the solvent was evaporated under reduced pressure. The crude product was recrystallized from methanol (100 mL) until the solid showed a constant optical rotation (three times are sufficient). Enantiomerically pure product (+)-8 (540 mg, 1.51 mmol, 79%) could be obtained as a colorless solid (decomp. 250 °C).  $[a]_{D}^{20} = +18 (c = 1 \text{ g } \text{L}^{-1} \text{ in } \text{H}_2\text{O})$ . The supernatants of the above crystallizations were combined, (S,S)-1,2-diaminocyclohexane (217 mg, 1.90 mmol) was added, and the resulting mixture evaporated. The residue was recrystallized twice from methanol (100 mL) to yield enantiomerically pure (-)-8 (456 mg, 1.27 mmol, 67%) as a colorless solid (decomp. 250 °C).  $[a]_{D}^{20} = -15$  (c = 1 gL<sup>-1</sup> in H<sub>2</sub>O). <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O):  $\delta =$ 3.65 (d, J = 4.9 Hz, 2 H), 3.57-3.35 (m, 2 H), 2.32-2.23 (m, 4 H),2.23-2.11 (m, 2 H), 1.99-1.89 (m, 2 H), 1.86-1.75 (m, 2 H), 1.71-1.58 (m, 4 H), 1.53–1.41 (m, 2 H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz,  $D_2O$ :  $\delta$  = 55.18 (CH), 52.28 (CH), 29.33 (CH<sub>2</sub>), 22.81 (CH<sub>2</sub>), 22.11 (CH<sub>2</sub>), 19.68 (CH<sub>2</sub>) ppm. IR (ATR):  $\tilde{v} = 3375$  (br), 2923 (m), 2759 (m), 2208 (w), 1584 (w), 1519 (w), 1455 (w), 1404 (w), 1208 (s), 1171 (vs), 1053 (s), 1034 (vs), 986 (m), 911 (w), 879 (w), 825 (w), 762 (m), 731 (w), 628 (m), 613 (s), 542 (s) cm<sup>-1</sup>.  $C_{12}H_{26}N_2O_6S_2$ (358.47): calcd. C 40.21, H 7.31, N 7.81, S 17.89; found C 40.21, H 7.56, N 7.52, S 18.11. Single crystals of compound (+)-8 suitable for X-ray analysis were obtained by slow evaporation of a solution in water.

(+)-(S,S)-1,2-Cyclohexanedisulfonic Acid Dihydrate [(+)-3]: Compound (+)-8 (387 mg, 1.08 mmol) was dissolved in water (20 mL) and transferred on top of a column (20 g, Amberlyst 15). The acid was eluted with water until the pH of the eluent was neutral (ca. 80 mL). After removal of the water by rotary evaporation and drying of the residue under high vacuum, the title compound (+)-3 (303 mg, 1.08 mmol, 100%) was obtained as a strongly hygroscopic, colorless solid.  $[a]_{D}^{20} = +37$  ( $c = 1 \text{ gL}^{-1}$  in H<sub>2</sub>O). <sup>1</sup>H NMR  $(500 \text{ MHz}, D_2 \text{O}): \delta = 3.56 \text{ (br. d}, J = 5.8 \text{ Hz}, 2 \text{ H}), 2.17 \text{ (br. d}, J$ = 14.5 Hz, 2 H), 2.12–2.01 (m, 2 H), 1.77–1.64 (m, 2 H), 1.58–1.50 (m, 2 H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, D<sub>2</sub>O):  $\delta$  = 55.08 (CH), 21.99 (CH<sub>2</sub>), 19.59 (CH<sub>2</sub>) ppm. IR (ATR):  $\tilde{v} = 2953$  (m), 2928 (m), 2876 (m), 2441 (br), 2166 (br), 1780 (br), 1453 (w), 1312 (w), 1290 (w), 1260 (w), 1160 (m), 1084 (s), 1030 (s), 994 (s), 913 (m), 854 (m), 810 (m), 732 (m), 682 (m), 644 (w), 589 (m) cm<sup>-1</sup>. MS (ESI, pos.):  $m/z = 245 [M + H^+], 277 [M + Na^+]. C_6H_{12}O_6S_2 \cdot 2H_2O$ (280.31): calcd. C 25.71, H 5.75, S 22.88; found C 25.49, H 5.74, S 22.77.

(-)-(*R*,*R*)-1,2-Cyclohexanedisulfonic Acid Dihydrate [(-)-3]: This compound was obtained in analogy to its enantiomer (+)-3 using (-)-8 (80 mg, 223 µmol) as starting material. The product (-)-3 (62 mg, 221 µmol, 99%) could be obtained as a strongly hygroscopic, colorless solid.  $[a]_{D}^{2D} = -43$  (*c* = 1 g L<sup>-1</sup> in H<sub>2</sub>O).

(-)-Disodium (*R*,*R*)-1,2-Cyclohexanedisulfonate·1.8H<sub>2</sub>O [(-)-9]: NaHCO<sub>3</sub> (37 mg, 435 µmol) was added to a solution of sulfonic acid (-)-(*R*,*R*)-3 (62 mg, 223 µmol) in water (5 mL). Colorless crystals (71 mg, 221 µmol, 99%) suitable for X-ray analysis could be obtained by slow evaporation of the solvent at ambient temperature.  $[a]_{D}^{2D} = -22$  ( $c = 1 \text{ g L}^{-1}$  in H<sub>2</sub>O).

(Dimethylammonium) Silver(I) (R,R)-1,2-Cyclohexanedisulfonate [(R,R)-10]: A glass ampoule was filled with Ag<sub>2</sub>CO<sub>3</sub> (44 mg, 0.16 mmol), (–)-(R,R)-3 (30 mg, 0.11 mmol), and DMF (2.5 mL) and it was torch-sealed under vacuum. The ampoule was placed in a resistance furnace and heated up to 105 °C within 6 h. After 24 h the furnace was slowly cooled to room temperature within 96 h. The product was obtained as transparent single crystals in approximately 60% yield with respect to the initial Ag<sub>2</sub>CO<sub>3</sub>. They were separated from the supernatant by decantation.

Supporting Information (see footnote on the first page of this article):  ${}^{1}$ H and  ${}^{13}C{}^{1}$ H NMR spectra of all products.

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