

## Poly[triaqua( $\mu_4$ -4-carboxybenzene-sulfonato- $\kappa^4$ O':O':O'':O''')(4-carboxybenzenesulfonato- $\kappa$ O)strontium(II)]

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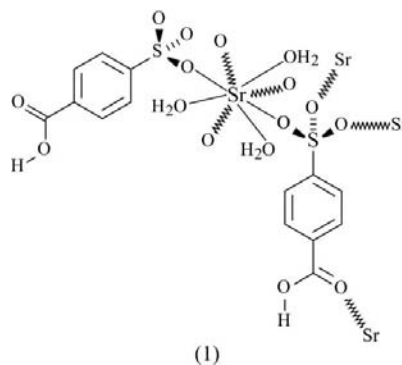
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This study presents the coordination modes and two-dimensional network of a novel strontium(II) coordination polymer,  $[\text{Sr}(\text{C}_7\text{H}_5\text{O}_5\text{S})_2(\text{H}_2\text{O})_3]_n$ . The eight-coordinate  $\text{Sr}^{2+}$  ion is in a distorted bis-disphenoidal coordination environment, surrounded by four sulfonate and one carboxyl O atom from five benzenesulfonate ligands, two of which are symmetry unique, and by three O atoms from three independent aqua ligands. The compound exhibits a monolayer structure with coordination bonds within and hydrogen bonds between the layers. The  $\mu_4$  acid ligand bridges the metal ions in two dimensions to form a thick undulating monolayer with a hydrophobic interior and hydrophilic surfaces. A second independent monoanion is arranged outward from both sides of the monolayer and serves to link adjacent monolayers *via* carboxyl–water and water–carboxyl hydrogen bonds.

### Comment

Hybrid inorganic–organic layered compounds are of interest for their potential applications in chemical separation, gas sorption, sensing and catalysis (Clearfield, 1998; Alberti & Constanino, 1996; Kong *et al.*, 2006; Sharma & Clearfield, 2000; Cabeza *et al.*, 2002). Aromatic dicarboxylic acids with *endo*-positioned functional groups, especially terephthalic acid, are widely exploited as bridging ligands and organic linkers in order to form coordination polymers. Moreover, by controlling the geometry of the entities between the metal ions one can regulate the organization within layers and obtain different structures. In this context, the monosubstituted sulfonic analogues of terephthalic acid merit special attention. The ligand 4-sulfobenzoic acid has the potential to bind metal ions with variable coordination modes (from  $\eta^1\mu_1$  to  $\eta^{10}\mu_9$ ), which can lead to high-dimensional networks and structurally diverse compounds (Videnova-Adrabsinska, 2007; Prochniak *et al.*, 2008). The lack of symmetry in the organic linker is a useful attribute of the ligand since this may lead to structural variation in the interlayer region. However, most of the 28

4-sulfobenzoate compounds retrieved from the Cambridge Structural Database (Version 5.29; Allen, 2002) contain chelating auxiliary ligands, obviating higher-dimensional aggregation of the ions. Only two compounds, *catena*- $[(\mu_4$ -benzene-1,4-disulfonato)bis( $\mu_4$ -4-sulfobenzoato)bis( $\mu_2$ -aqua)aquadi-europium(III)] and *catena*- $[(\mu_4$ -benzene-1,4-disulfonato)bis( $\mu_4$ -4-sulfobenzoato)bis( $\mu_2$ -aqua)aquadigadolinium(III)], were found to have a layered structure, but they incorporate an additional 1,4-disulfonate ligand (Xiong *et al.*, 2001). We report here the crystal structure of  $[\text{Sr}(4\text{-sb})_2(\text{H}_2\text{O})_3]_n$  (1), where 4-sb is 4-carboxybenzenesulfonate.



The asymmetric unit of (1) consists of one Sr atom, two independent monodeprotonated 4-sb anions and three water molecules. The coordination environment of the metal center consists of four sulfonate and one carboxyl group, from five different acid monoanions (two of which are symmetry unique), and three water molecules. The  $\text{SrO}_8$  coordination polyhedron (Fig. 1) is strongly deformed and intermediate between an antiprism (sap) with a face symbol  $[3^8.4^2]$  (see <http://rcsr.anu.edu.au>) and a bis-disphenoid (bds,  $[3^{12}]$ ). The coordination bonds range between 2.496 (1) and 2.738 (1) Å (Table 1). One of the acid monoanions mediates the arrangement of the metal ions into a thick monolayer, while the second independent anion serves to crosslink the monolayers. The sulfonate site of the first monoanion bridges, in a  $\mu_3$  fashion, the strontium ions along the *c* axis in order to form coordination ribbons. The Sr1–O41 and Sr1–O42<sup>ii</sup> bonds bridge the metal centers into a *C*(4) chain, and the Sr–O43<sup>i</sup> bond interweaves two *c*-glide chains into a ribbon (all symmetry codes are as given in Tables 1 and 2) An *R*2,4(8) ring motif is generated along the ribbon. [For a topological

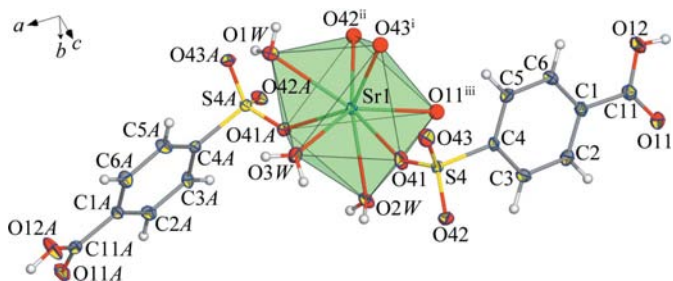
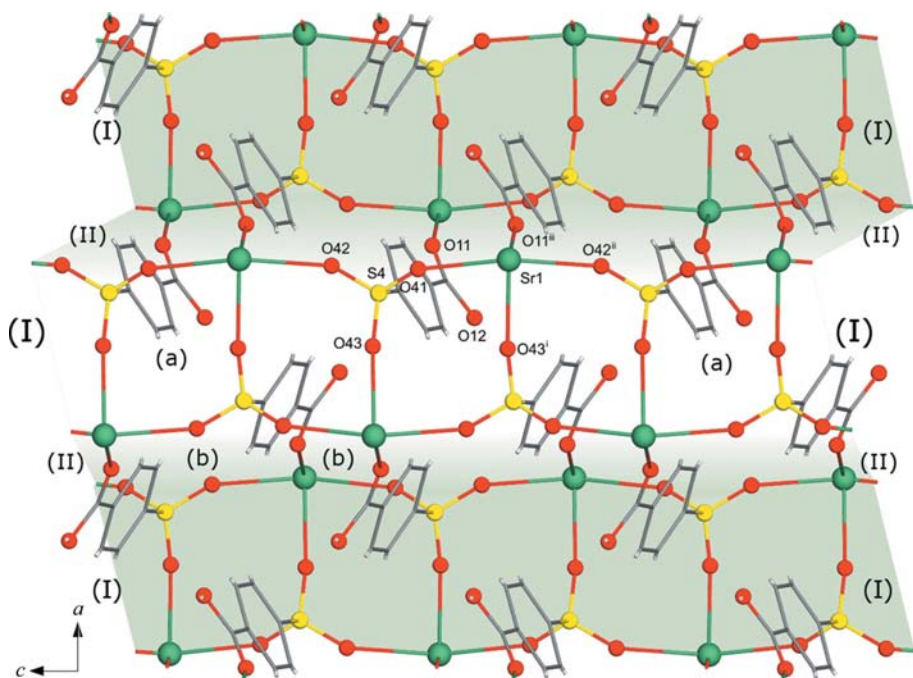


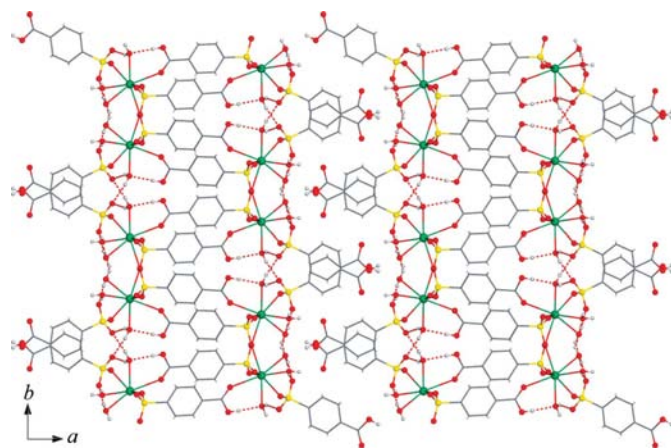
Figure 1

A view of the coordination unit and the coordination polyhedron of the title compound. Displacement ellipsoids are shown at the 50% probability level. Symmetry codes are as given in Table 1.


**Figure 2**

A view of the pleated two-dimensional network in (1). The alternating ribbons (light and dark arranged at the top and bottom of the picture) form the outer surfaces (I), while the aromatic linkers between them occupy the interior (II) of the monolayer. The different types of coordination ring motifs characterizing the network are assigned as (a)  $R2,4(8)$  and (b)  $R2,4(18)$ . For the sake of clarity, the nonbridging acid ligand and the three aqua ligands are not shown. Symmetry codes are as given in Table 1.

description of the motifs, see Videnova-Adrabska (2007). The aromatic rings are arrayed on both sides of the ribbons. The distal carboxyl groups serve to link neighboring inversion-related ribbons *via* the Sr—O11<sup>iii</sup> bond, in order to form an undulating monolayer with a hydrophobic interior and hydrophilic surfaces (Fig. 2). The two-dimensional network of the monolayer is girded with smaller ring motifs [ $R2,4(8)$ ] along the ribbons and larger motifs [ $R2,4(18)$ ] between the ribbons, where the aqua ligands and the benzene rings reside.


**Figure 3**

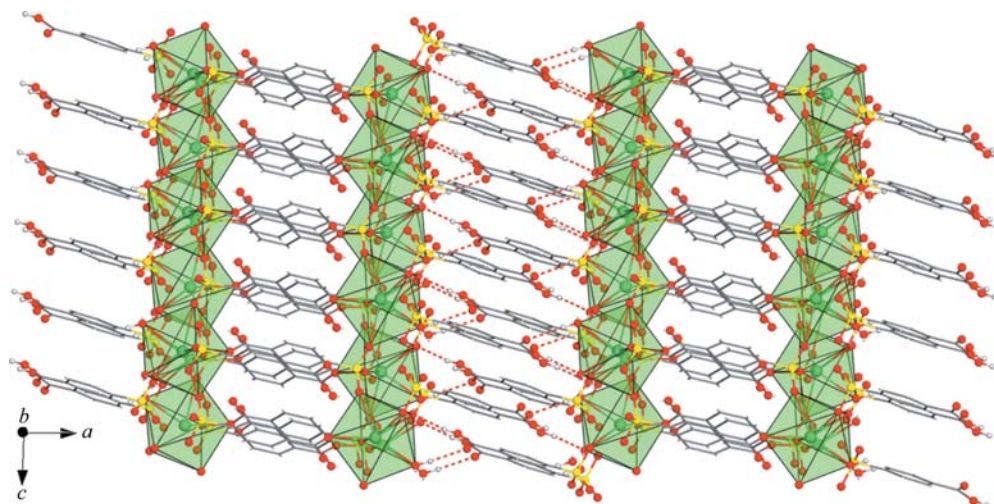
A side view of two adjacent monolayers presenting the different intra- and interlayer relations. For the sake of clarity, the hydrogen bonds interlinking the monolayers and the H atoms on the aromatic rings have been omitted.

The aromatic rings of the  $\mu_4$  ligands play the role of linkers between the ribbons and are arranged in the interior of the monolayer with offset face-to-face (OFF) interactions.

The second independent acid anion (atom labels ending with *A*) is bonded to strontium in a monodentate fashion (Sr—O41*A*) and arranged outward from both sides of the monolayer (Fig. 3). The aromatic portions of the *A* ligands protrude into the interlayer regions and are organized into stacks along the *c* axis. The rings along the stack are *c*-glide-related, with a distance of 3.735 (1) Å between their centers of gravity. The aqua ligands serve to complete the coordination environment of the strontium ion and to stabilize the monolayer structure. A carboxyl–water hydrogen bond (O12—H12···O2W<sup>iii</sup>) stabilizes the interior of the monolayer. Four more hydrogen-bonds [O1W—H2W···O43*A*, O2W—H3W···O42*A*<sup>v</sup>, O2W—H4W···O42*A*<sup>vi</sup> and O3W—H6W···O43*A*<sup>vi</sup>; O···O = 2.743 (2)–2.7717 (19) Å], established between the water molecules and the sulfonate O

atoms of the *A* ligands, contribute to the layer folding. The distal carboxyl groups of the *A* ligands are used to connect the monolayers *via* hydrogen-bond interactions (Fig. 4). Two relatively strong hydrogen bonds, O12*A*—H12*A*···O1W<sup>iv</sup> and O3W—H5W···O11*A*<sup>vii</sup>, formed between the carboxyl groups of one layer and the aqua ligands of the next layer, crosslink the monolayers. There are no aromatic interactions between the stacks of adjacent monolayers. Interlayer interactions (C2*A*—H2*A*···O11*A*<sup>viii</sup> and C5*A*—H5*A*···O11*A*<sup>vii</sup>, Table 2) are established between the aromatic rings and the carbonyl O atoms. The crystal packing involves segregation of hydrophilic and hydrophobic regions alternating along the crystallographic *a* axis. The hydrophilic regions contain the metal ions and the functional groups of the ligands. All coordination and hydrogen bonds occur here. However, the hydrophobic regions on opposite sides of the hydrophilic region are different: the benzene rings (the organic linkers) on one side are organized with intralayer OFF interactions and on the other side with FF interactions.

Finally, it seems useful to compare this polymeric structure with that of [Sr(terephthalate)(H<sub>2</sub>O)<sub>4</sub>] (Groeneman & Atwood, 1999). Only one of the end-positioned functional groups of the terephthalate dianion serves as a ligand and it bridges the strontium ions with a  $\mu_2$ -mode in order to form coordination strands. The second carboxylate site bears a negative charge, and the ribbons are held together by numerous water–carboxylate hydrogen bonds and  $\pi$ – $\pi$  interactions. Hence, this compound exhibits a one-dimensional coordination network instead of a monolayer structure.

**Figure 4**

A view along the *b* axis, showing the hydrophilic–hydrophobic segregation in the crystal structure, as well as the dissimilarities in ring organization and connectivity patterns on opposite sides of the coordination region.

## Experimental

The title compound was synthesized by dissolving potassium 1-carboxybenzenesulfonate (2.08 mmol) and strontium chloride hexahydrate (1.04 mmol) in distilled water (4 ml). The mixture was sealed in a glass vial and heated at 353 K for 4 h and then cooled slowly at a rate of 1.25 K h<sup>-1</sup> to room temperature. Needle-shaped crystals suitable for X-ray measurements were retrieved after the cooling process.

### Crystal data

[Sr(C <sub>7</sub> H <sub>5</sub> O <sub>5</sub> S) <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ]	<i>V</i> = 1912.9 (3) Å <sup>3</sup>
<i>M<sub>r</sub></i> = 544.01	<i>Z</i> = 4
Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 22.5926 (4) Å	<i>μ</i> = 3.11 mm <sup>-1</sup>
<i>b</i> = 11.7646 (2) Å	<i>T</i> = 183 (2) K
<i>c</i> = 7.2025 (11) Å	0.22 × 0.07 × 0.05 mm
<i>β</i> = 92.221 (2)°	

### Data collection

Oxford Diffraction Xcalibur diffractometer	17871 measured reflections
Absorption correction: multi-scan ( <i>CrysAlis RED</i> ; Oxford Diffraction, 2008)	5831 independent reflections
<i>T</i> <sub>min</sub> = 0.548, <i>T</i> <sub>max</sub> = 0.860	4046 reflections with <i>I</i> > 2σ( <i>I</i> )
	<i>R</i> <sub>int</sub> = 0.041

### Refinement

<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] = 0.030	H atoms treated by a mixture of independent and constrained refinement
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.050	Δ <i>ρ</i> <sub>max</sub> = 0.47 e Å <sup>-3</sup>
<i>S</i> = 0.89	Δ <i>ρ</i> <sub>min</sub> = -0.51 e Å <sup>-3</sup>
5831 reflections	
295 parameters	
1 restraint	

The H atoms of the carboxyl groups and the water molecules were located in difference Fourier maps and placed at calculated sites. One restraint was used for the O1*W*–H1*W* distance. The H atoms of the aromatic ring were placed at calculated positions. All H atoms were refined with *U*<sub>iso</sub>(H) values correlated with the *U*<sub>eq</sub> values of the atoms to which they are bonded.

**Table 1**

Selected geometric parameters (Å, °).

Sr1–O43 <sup>i</sup>	2.4956 (14)	S4–O41	1.4439 (13)
Sr1–O41 <i>A</i>	2.5342 (12)	S4–O42	1.4454 (13)
Sr1–O42 <sup>ii</sup>	2.5343 (13)	S4–O43	1.4486 (15)
Sr1–O3 <i>W</i>	2.5430 (15)	S4–C4	1.7739 (18)
Sr1–O41	2.5517 (13)	S4 <i>A</i> –O41 <i>A</i>	1.4499 (13)
Sr1–O11 <sup>iii</sup>	2.5719 (13)	S4 <i>A</i> –O42 <i>A</i>	1.4553 (13)
Sr1–O2 <i>W</i>	2.6829 (15)	S4 <i>A</i> –O43 <i>A</i>	1.4575 (13)
Sr1–O1 <i>W</i>	2.7382 (14)	S4 <i>A</i> –C4 <i>A</i>	1.7731 (19)
O43 <sup>i</sup> –Sr1–O41 <i>A</i>	143.85 (4)	O42 <sup>ii</sup> –Sr1–O41	145.55 (4)
O43 <sup>i</sup> –Sr1–O42 <sup>ii</sup>	82.43 (4)	O43 <sup>i</sup> –Sr1–O11 <sup>iii</sup>	92.41 (5)
O41 <i>A</i> –Sr1–O42 <sup>ii</sup>	77.13 (4)	O41 <i>A</i> –Sr1–O11 <sup>iii</sup>	109.84 (4)
O43 <sup>i</sup> –Sr1–O41	77.93 (4)	O42 <sup>ii</sup> –Sr1–O11 <sup>iii</sup>	74.05 (4)
O41 <i>A</i> –Sr1–O41	132.96 (4)	O41–Sr1–O11 <sup>iii</sup>	78.76 (4)

Symmetry codes: (i) *x*, –*y* +  $\frac{3}{2}$ , *z* –  $\frac{1}{2}$ ; (ii) *x*, *y*, *z* – 1; (iii) –*x* + 1, –*y* + 2, –*z* + 2.

**Table 2**

Hydrogen-bond geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O12 <i>A</i> –H12 <i>A</i> ...O1 <i>W</i> <sup>iv</sup>	0.81 (2)	1.89 (2)	2.692 (2)	168 (3)
O12–H12...O2 <i>W</i> <sup>iii</sup>	0.81 (2)	1.82 (2)	2.630 (2)	175 (3)
O1 <i>W</i> –H1 <i>W</i> ...O3 <i>W</i> <sup>i</sup>	0.756 (15)	2.362 (18)	3.003 (2)	143 (2)
O1 <i>W</i> –H2 <i>W</i> ...O43 <i>A</i>	0.87 (2)	1.90 (2)	2.743 (2)	165 (2)
O2 <i>W</i> –H3 <i>W</i> ...O42 <i>A</i> <sup>v</sup>	0.83 (2)	1.93 (2)	2.7550 (19)	172 (2)
O2 <i>W</i> –H4 <i>W</i> ...O42 <i>A</i> <sup>vi</sup>	0.78 (2)	2.01 (2)	2.7717 (19)	163 (2)
O3 <i>W</i> –H5 <i>W</i> ...O11 <i>A</i> <sup>vii</sup>	0.80 (2)	2.03 (2)	2.8220 (19)	170 (2)
O3 <i>W</i> –H6 <i>W</i> ...O43 <i>A</i> <sup>vi</sup>	0.82 (2)	1.94 (2)	2.7579 (19)	174 (2)
C5 <i>A</i> –H5 <i>A</i> ...O11 <i>A</i> <sup>vii</sup>	0.95	2.56	3.162 (3)	122
C2 <i>A</i> –H2 <i>A</i> ...O11 <i>A</i> <sup>viii</sup>	0.95	2.50	3.378 (3)	153

Symmetry codes: (i) *x*, –*y* +  $\frac{3}{2}$ , *z* –  $\frac{1}{2}$ ; (iii) –*x* + 1, –*y* + 2, –*z* + 2; (iv) –*x* + 2, *y* +  $\frac{1}{2}$ , –*z* +  $\frac{3}{2}$ ; (v) *x*, –*y* +  $\frac{3}{2}$ , *z* +  $\frac{1}{2}$ ; (vi) *x*, *y*, *z* + 1; (vii) –*x* + 2, *y* –  $\frac{1}{2}$ , –*z* +  $\frac{3}{2}$ ; (viii) –*x* + 2, –*y* + 3, –*z* + 1.

Data collection, cell refinement and data reduction: *CrysAlisPro* (Oxford Diffraction, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2008); software used to prepare material for publication: *PLATON* (Spek 2003) and *pubCIF* (Westrip, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3171). Services for accessing these data are described at the back of the journal.

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