# metal-organic papers

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#### **Key indicators**

Single-crystal X-ray study T = 93 KMean  $\sigma(C-C) = 0.004 \text{ Å}$  R factor = 0.031 wR factor = 0.091 Data-to-parameter ratio = 11.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

# Tetrasodium tetrahydroxytetrathiacalix[4]arenetetrasulfonate tetradecahydrate

The title compound,  $4Na^+ \cdot C_{24}H_{12}O_{16}S_8^{4-} \cdot 14H_2O$  (Na<sub>4</sub>TCAS-14H<sub>2</sub>O), was found to crystallize in the triclinic space group  $P\overline{1}$ . The X-ray structure revealed that the centrosymmetric TCAS<sup>4-</sup> anion adopts the 1,2-alternate conformation. The sodium cations are surrounded by five or six O atoms in the crystal structure. All sodium ions form centrosymmetric aquabridged dimers, Na( $\mu$ -H<sub>2</sub>O)<sub>2</sub>Na, which are also coordinated by sulfonate O atoms and contribute to the formation of a three-dimensional network. The compound exists in the solid state as layers of anionic thiacalixarenes, alternating with inorganic layers that contain sodium cations and water molecules. Intercalation of metal ions into the solid-state layered structure was observed.

#### Comment

The title compound, (I) ( $Na_4TCAS \cdot 14H_2O$ ), affords the first crystal structure of  $Na_4TCAS$  without organic solvents as guest molecules, while crystal structures of  $Na_4TCAS$  with acetone or 1,4-dioxane (Iki *et al.*, 2001) and an analog of thiacalix[4]arenetetrasulfonate,  $Na_5[S_8C_{24}O_{24}H_{11}]$ ·EtOH·-9H<sub>2</sub>O (Iki *et al.*, 2002), are already known.



A view of the TCAS<sup>4–</sup> anion is shown in Fig. 1. Selected bond distances and angles are given in Table 1. The TCAS<sup>4–</sup> anion adopts the 1,2-alternate conformation. The anion lies on an inversion center. The center of symmetry resides on the mid-point of two S atoms (S1 and S1\*). The bond distances and angles in the TCAS<sup>4–</sup> anion are similar to those observed in Na<sub>4</sub>[C<sub>24</sub>H<sub>12</sub>O<sub>16</sub>S<sub>8</sub>]·2C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>·9H<sub>2</sub>O (Iki *et al.*, 2001).

The environments around the ions Na1 and Na2 are different. The Na1 ion is coordinated by six O atoms (O2 and  $O6^{ii}$  from sulfonate O atoms, and O9, O10, O11 and O11<sup>iii</sup> from water molecules; see Table 1 for symmetry codes) in a distorted octahedral manner. The NaO<sub>6</sub> polyhedra share a common edge. The bridging positions are occupied by water molecules (O11 and O11<sup>iii</sup>). A center of symmetry lies at the

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ORTEP-3 drawing of the TCAS<sup>4–</sup> anion, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 80% probability level and H atoms are shown as spheres of arbitrary radii. Atoms marked with an asterisk are related to those without an asterisk by a center of symmetry.

midpoint of the two aqua-bridges. The Na1···O11 [2.346 (2) Å] and Na1···O11<sup>iii</sup> [2.474 (2) Å] distances are in the range of the usual Na··· $\mu$ -H<sub>2</sub>O distances (2.35–2.48 Å) [for examples see Dressick *et al.* (2000) and Achour *et al.* (1998)]. The Na2 ion is coordinated by five O atoms (O3 and O8<sup>iv</sup> from sulfonate O atoms, and O12, O13 and O13<sup>v</sup> from water molecules; see Table 1 for symmetry codes) in a distorted trigonal bipyramidal manner. The NaO<sub>5</sub> polyhedra share a common edge. The bridging positions are occupied by water molecules (O13 and O13<sup>v</sup>). A center of symmetry lies at the mid-point of the two aqua bridges. The Na2···O13 [2.388 (2) Å] and Na2···O13<sup>v</sup> [2.388 (2) Å] distances are in the usual range for Na··· $\mu$ -H<sub>2</sub>O distances (2.27–2.44 Å) [for examples see Hauptmann *et al.* (1999) and Jeon *et al.* (1996)].

The crystal structure of (I), viewed along the *b* axis, is shown in Fig. 2. Since sulfonate O atoms are coordinated to Na<sup>+</sup> cations, TCAS<sup>4–</sup> anions are further connected by sodium aqua dimers, Na $-(\mu$ -H<sub>2</sub>O)<sub>2</sub>-Na, forming a three-dimensional network.

The compound exists in the solid state as layers of anionic thiacalixarenes in the 1,2-alternate configuration, alternating with inorganic layers that contain sodium cations and water molecules. The overall structure bears a close resemblance to those found in clay minerals. This similarity has also been





Projection of the structure of compound (I) along the b axis. The C, O, Na and S atoms are drawn in black, red, blue and yellow, respectively. Non-coordinated water molecules have been omitted for clarity.

reported in studies of other calixarene compounds (Atwood et al., 1988; Coleman et al., 1988).

Several metal (Fe, Co, Ni, Cu, Zn) complexes of watersoluble thiacalix[4]arenetetrasulfonate have been prepared by the incorporation of the metal ions into the solid-state layered structure. There have also been several reports of the intercalation of metal ions with water-soluble calix[4]arenes (Atwood *et al.*, 1992). X-ray structure analyses of metal complexes of water-soluble thiacalix[4]arenetetrasulfonate are in progress.

## Experimental

A sample of sodium thiacalix[4]arenetetrasulfonate, (Na<sub>4</sub>TCAS), was obtained from Cosmo Oil Co. Ltd. Crystals suitable for single-crystal X-ray diffraction were recrystallized by adding sodium chloride to an aqueous solution of Na<sub>4</sub>(TCAS).

#### Crystal data

| $4Na^{+} \cdot C_{24}H_{12}O_{16}S_{8}^{4-} \cdot 14H_{2}O_{16}S_{8}^{4-} \cdot 1$ | Z = 1                                      |
|--|--|
| $M_r = 1157.00$  | $D_x = 1.730 \text{ Mg m}^{-3}$            |
| Triclinic, P1  | Mo K $\alpha$ radiation                    |
| a = 8.2974(7) Å  | Cell parameters from 4591                  |
| b = 8.8446 (6) Å   | reflections                                |
| c = 15.789(1)  Å   | $\theta = 2.5 - 27.5^{\circ}$              |
| $\alpha = 95.743 \ (4)^{\circ}$  | $\mu = 0.54 \text{ mm}^{-1}$               |
| $\beta = 102.490 \ (2)^{\circ}$  | T = 93.1  K                                |
| $\gamma = 97.897 \ (4)^{\circ}$  | Plate, colorless                           |
| $V = 1110.4 (1) \text{ Å}^3$   | $0.30 \times 0.20 \times 0.10 \text{ mm}$  |
| Data collection  |  |
| Rigaku R-AXIS-IV diffractometer  | 3541 reflections with $F^2 > 2\sigma(F^2)$ |
| ωscans   | $R_{\rm int} = 0.018$                      |
| Absorption correction: multi-scan  | $\theta_{\rm max} = 27.5^{\circ}$          |
| (Higashi, 1995)  | $h = -10 \rightarrow 10$                   |
| $T_{\min} = 0.848, \ T_{\max} = 0.948$   | $k = -11 \rightarrow 11$                   |
| 8541 measured reflections  | $l = -20 \rightarrow 20$                   |
| 4678 independent reflections   |  |

Refinement

| Refinement on $F^2$             | Only coordinates of H atoms                               |
|---------------------------------|---|
| $R[F^2 > 2\sigma(F^2)] = 0.031$ | refined   |
| $wR(F^2) = 0.091$               | $w = 1/[0.001F_o^2 + \sigma^2(F_o) + 0.5]$                |
| S = 0.84                        | $(4F_o^2)$  |
| 4233 reflections                | $(\Delta/\sigma)_{\rm max} < 0.001$                       |
| 358 parameters                  | $\Delta \rho_{\rm max} = 0.46 \ {\rm e} \ {\rm \AA}^{-3}$ |
|                                 | $\Delta \rho_{\rm min} = -0.54 \text{ e} \text{ Å}^{-3}$  |

#### Table 1

Selected geometric parameters (Å, °).

| S1-C6                      | 1.770 (2)   | C5-C6                                  | 1.386 (3)   |
|----------------------------|-------------|--|-------------|
| S1-C12                     | 1.769 (2)   | C7-C8                                  | 1.405 (3)   |
| S2-C2                      | 1.792 (2)   | C7-C12                                 | 1.398 (3)   |
| S2-C8 <sup>i</sup>         | 1.785 (2)   | C8-C9                                  | 1.393 (3)   |
| S3-O2                      | 1.4590 (18) | C9-C10                                 | 1.390 (3)   |
| \$3-03                     | 1.4524 (18) | C10-C11                                | 1.390 (3)   |
| S3-O4                      | 1.4715 (18) | C11-C12                                | 1.392 (3)   |
| S3-C4                      | 1.763 (2)   | Na1-O2                                 | 2.382 (2)   |
| S4-O6                      | 1.4590 (18) | Na1-O6 <sup>ii</sup>                   | 2.434 (2)   |
| S4-O7                      | 1.4635 (18) | Na1-O9                                 | 2.373 (2)   |
| S4-O8                      | 1.4593 (18) | Na1-O10                                | 2.531 (2)   |
| S4-C10                     | 1.772 (2)   | Na1-O11                                | 2.347 (2)   |
| O1-C1                      | 1.347 (3)   | Na1-O11 <sup>iii</sup>                 | 2.475 (2)   |
| O5-C7                      | 1.350 (3)   | Na2-O3                                 | 2.252 (2)   |
| C1-C2                      | 1.404 (4)   | Na2–O8 <sup>iv</sup>                   | 2.402 (2)   |
| C1-C6                      | 1.406 (3)   | Na2-O12                                | 2.292 (2)   |
| C2-C3                      | 1.395 (3)   | Na2-O13                                | 2.387 (2)   |
| C3-C4                      | 1.396 (3)   | Na2-O13 <sup>v</sup>                   | 2.423 (2)   |
| C4-C5                      | 1.383 (4)   |  |             |
| C6-S1-C12                  | 105.61 (11) | C8-C7-C12                              | 119.4 (2)   |
| $C2 - S2 - C8^{i}$         | 100.93 (11) | $S2^{i}-C8-C9$                         | 120.93 (18) |
| 02-\$3-03                  | 112.97 (11) | $S2^{i}-C8-C7$                         | 119.39 (18) |
| 02 - 83 - 04               | 111.40 (11) | C7 - C8 - C9                           | 119.6 (2)   |
| 03-83-04                   | 112.24 (11) | C8-C9-C10                              | 120.2(2)    |
| O2-S3-C4                   | 106.15 (11) | S4-C10-C9                              | 118.03 (18) |
| O3-S3-C4                   | 107.77 (11) | S4-C10-C11                             | 121.50 (18) |
| O4-S3-C4                   | 105.79 (11) | C9-C10-C11                             | 120.5 (2)   |
| O6-S4-O7                   | 112.21 (11) | C10-C11-C12                            | 119.5 (2)   |
| 06-\$4-08                  | 113.01 (11) | S1-C12-C7                              | 121.24 (18) |
| 07-\$4-08                  | 112.27 (11) | S1-C12-C11                             | 118.07 (18) |
| O6-S4-C10                  | 105.68 (11) | C7-C12-C11                             | 120.6 (2)   |
| O7-S4-C10                  | 106.04 (11) | O2-Na1-O6 <sup>ii</sup>                | 85.21 (7)   |
| O8-S4-C10                  | 107.00 (11) | O2-Na1-O9                              | 166.16 (8)  |
| \$3-O2-Na1                 | 134.69 (11) | O2-Na1-O10                             | 104.32 (7)  |
| \$3-O3-Na2                 | 148.88 (12) | O2-Na1-O11                             | 88.49 (7)   |
| S4-O6-Na1 <sup>ii</sup>    | 149.38 (11) | O2-Na1-O11 <sup>iii</sup>              | 79.91 (7)   |
| S4-O8-Na2 <sup>iv</sup>    | 127.9 (1)   | O6 <sup>ii</sup> -Na1-O9               | 81.28 (7)   |
| Na1-O11-Na1 <sup>iii</sup> | 96.80(7)    | O9-Na1-O10                             | 76.97 (7)   |
| Na2-O13-Na2 <sup>v</sup>   | 94.18 (7)   | O9-Na1-O11                             | 95.64 (7)   |
| O1-C1-C2                   | 124.1 (2)   | O9-Na1-O11 <sup>iii</sup>              | 113.65 (7)  |
| O1-C1-C6                   | 116.6 (2)   | O10-Na1-O11                            | 155.35 (8)  |
| C2-C1-C6                   | 119.3 (2)   | O11-Na1-O11 <sup>iii</sup>             | 83.20 (7)   |
| S2-C2-C1                   | 119.80 (18) | \$3-Na2-O12                            | 165.22 (6)  |
| S2-C2-C3                   | 119.92 (19) | O3-Na2-O12                             | 153.71 (8)  |
| C1-C2-C3                   | 120.2 (2)   | O3-Na2-O13                             | 87.89 (7)   |
| C2-C3-C4                   | 119.4 (2)   | O3-Na2-O8 <sup>iv</sup>                | 87.03 (7)   |
| S3-C4-C3                   | 120.07 (19) | O3-Na2-O12                             | 153.71 (8)  |
| \$3-C4-C5                  | 118.89 (19) | $O3-Na2-O13^{v}$                       | 102.85 (7)  |
| C3-C4-C5                   | 120.9 (2)   | O8 <sup>iv</sup> -Na2-O12              | 87.12 (7)   |
| C4-C5-C6                   | 120.1 (2)   | O8 <sup>iv</sup> -Na2-O13              | 143.44 (7)  |
| S1-C6-C1                   | 122.96 (18) | O8 <sup>iv</sup> -Na2-O13 <sup>v</sup> | 130.56 (7)  |
| S1-C6-C5                   | 116.68 (19) | O12-Na2-O13                            | 81.71 (7)   |
| C1-C6-C5                   | 120.1 (2)   | O12-Na2-O13 <sup>v</sup>               | 100.41 (7)  |
| O5-C7-C8                   | 123.5 (2)   | O13-Na2-O13 <sup>v</sup>               | 85.82 (7)   |
| O5-C7-C12                  | 117.0 (2)   |  | . /         |

Symmetry codes: (i) -x, -y, 1-z; (ii) 1-x, 1-y, 1-z; (iii) 1-x, -y, -z; (iv) 1-x, -y, 1-z; (v) -x, -1-y, -z.

# Table 2Hydrogen-bonding geometry (Å, °).

| $D - H \cdot \cdot \cdot A$ | D-H  | $H \cdot \cdot \cdot A$ | $D \cdots A$ | $D - H \cdots A$ |
|-----------------------------|------|-------------------------|--------------|------------------|
| 01-H1···015 <sup>iv</sup>   | 0.90 | 1.95                    | 2.693 (2)    | 140              |
| O5-H4···O15 <sup>vi</sup>   | 0.82 | 1.97                    | 2.688 (2)    | 146              |
| O9−H7···O4 <sup>vii</sup>   | 0.90 | 1.97                    | 2.831 (3)    | 159              |
| O9−H8···O14 <sup>vii</sup>  | 0.90 | 1.86                    | 2.756 (3)    | 176              |
| O10−H9···O4 <sup>vii</sup>  | 0.90 | 2.16                    | 3.033 (3)    | 166              |
| O10−H9···O9                 | 0.90 | 2.71                    | 3.055 (3)    | 104              |
| $O10-H10\cdots O7^{iv}$     | 0.90 | 2.06                    | 2.939 (3)    | 165              |
| O11-H11···O3 <sup>iii</sup> | 0.90 | 2.06                    | 2.894 (2)    | 153              |
| $O11-H12\cdots O12^{viii}$  | 0.90 | 2.07                    | 2.858 (3)    | 146              |
| $O12-H13\cdots O2^{ix}$     | 0.90 | 1.91                    | 2.796 (3)    | 171              |
| $O12-H14\cdots O4^{vi}$     | 0.90 | 1.90                    | 2.793 (3)    | 170              |
| $O13-H15\cdots O7^{x}$      | 0.90 | 2.04                    | 2.935 (3)    | 173              |
| O13−H16···O9 <sup>iii</sup> | 0.90 | 1.93                    | 2.787 (3)    | 159              |
| O14-H17···O5                | 0.90 | 2.04                    | 2.910 (3)    | 163              |

Symmetry codes: (iii) 1 - x, -y, -z; (iv) 1 - x, -y, 1 - z; (v) -x, -1 - y, -z; (vi) x - 1, y, z; (vii) 1 + x, y, z; (viii) x, 1 + y, z; (ix) x, y - 1, z; (x) x, y - 1, z - 1.

The positional parameters for all H atoms were initially located from a difference map. The coordinate parameters for all H atoms are refined. All water O–H distances and H–O–H angles were restrained to be 0.9 Å and 104°, respectively. The isotropic displacement parameters for all H atoms were fixed at 1.2 times the value of the equivalent isotropic displacement parameter of their carrier atom.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/ MSC, 2001); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *CrystalStructure*; molecular graphics: *ORTEP3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure*.

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