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Key indicators

Single-crystal X-ray study
 $T = 93$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.031
 wR factor = 0.091
Data-to-parameter ratio = 11.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Tetrasodium tetrahydroxytetrahiacalix[4]-arenetetrasulfonate tetradecahydrate

The title compound, $4\text{Na}^+ \cdot \text{C}_{24}\text{H}_{12}\text{O}_{16}\text{S}_8^{4-} \cdot 14\text{H}_2\text{O}$ ($\text{Na}_4\text{TCAS} \cdot 14\text{H}_2\text{O}$), was found to crystallize in the triclinic space group $P\bar{1}$. The X-ray structure revealed that the centrosymmetric TCAS^{4-} 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 aqua-bridged dimers, $\text{Na}(\mu\text{-H}_2\text{O})_2\text{Na}$, 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.

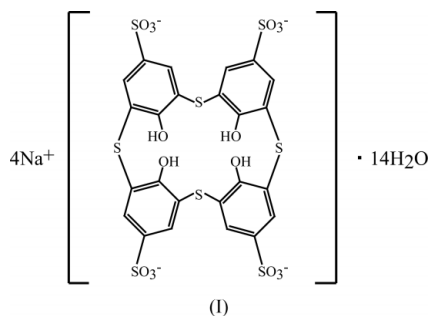
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Comment

The title compound, (I) ($\text{Na}_4\text{TCAS} \cdot 14\text{H}_2\text{O}$), 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, $\text{Na}_5[\text{S}_8\text{C}_{24}\text{O}_{24}\text{H}_{11}] \cdot \text{EtOH} \cdot 9\text{H}_2\text{O}$ (Iki *et al.*, 2002), are already known.



A view of the TCAS^{4-} anion is shown in Fig. 1. Selected bond distances and angles are given in Table 1. The TCAS^{4-} 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^{4-} anion are similar to those observed in $\text{Na}_4[\text{C}_{24}\text{H}_{12}\text{O}_{16}\text{S}_8] \cdot 2\text{C}_4\text{H}_8\text{O}_2 \cdot 9\text{H}_2\text{O}$ (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 O6ⁱⁱ from sulfonate O atoms, and O9, O10, O11 and O11ⁱⁱⁱ from water molecules; see Table 1 for symmetry codes) in a distorted octahedral manner. The NaO_6 polyhedra share a common edge. The bridging positions are occupied by water molecules (O11 and O11ⁱⁱⁱ). A center of symmetry lies at the

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.091$
 $S = 0.84$
 4233 reflections
 358 parameters

Only coordinates of H atoms refined
 $w = 1/[0.001F_o^2 + \sigma^2(F_o) + 0.5]$
 $(4F_o^2)$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.46 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.54 \text{ e } \text{\AA}^{-3}$

Table 1
 Selected geometric parameters (\AA , $^\circ$).

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 ⁱ	1.785 (2)	C8—C9	1.393 (3)
S3—O2	1.4590 (18)	C9—C10	1.390 (3)
S3—O3	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 ⁱⁱ	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 ⁱⁱⁱ	2.475 (2)
O5—C7	1.350 (3)	Na2—O3	2.252 (2)
C1—C2	1.404 (4)	Na2—O8 ^{iv}	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 ^v	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)
O2—S3—O3	112.97 (11)	S2 ⁱ —C8—C7	119.39 (18)
O2—S3—O4	111.40 (11)	C7—C8—C9	119.6 (2)
O3—S3—O4	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)
O6—S4—O8	113.01 (11)	S1—C12—C7	121.24 (18)
O7—S4—O8	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 ⁱⁱ	85.21 (7)
O8—S4—C10	107.00 (11)	O2—Na1—O9	166.16 (8)
S3—O2—Na1	134.69 (11)	O2—Na1—O10	104.32 (7)
S3—O3—Na2	148.88 (12)	O2—Na1—O11	88.49 (7)
S4—O6—Na1 ⁱⁱ	149.38 (11)	O2—Na1—O11 ⁱⁱⁱ	79.91 (7)
S4—O8—Na2 ^{iv}	127.9 (1)	O6 ⁱⁱ —Na1—O9	81.28 (7)
Na1—O11—Na1 ⁱⁱⁱ	96.80 (7)	O9—Na1—O10	76.97 (7)
Na2—O13—Na2 ^v	94.18 (7)	O9—Na1—O11	95.64 (7)
O1—C1—C2	124.1 (2)	O9—Na1—O11 ⁱⁱⁱ	113.65 (7)
O1—C1—C6	116.6 (2)	O10—Na1—O11	155.35 (8)
C2—C1—C6	119.3 (2)	O11—Na1—O11 ⁱⁱⁱ	83.20 (7)
S2—C2—C1	119.80 (18)	S3—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 ^{iv}	87.03 (7)
S3—C4—C3	120.07 (19)	O3—Na2—O12	153.71 (8)
S3—C4—C5	118.89 (19)	O3—Na2—O13 ^v	102.85 (7)
C3—C4—C5	120.9 (2)	O8 ^{iv} —Na2—O12	87.12 (7)
C4—C5—C6	120.1 (2)	O8 ^{iv} —Na2—O13	143.44 (7)
S1—C6—C1	122.96 (18)	O8 ^{iv} —Na2—O13 ^v	130.56 (7)
S1—C6—C5	116.68 (19)	O12—Na2—O13	81.71 (7)
C1—C6—C5	120.1 (2)	O12—Na2—O13 ^v	100.41 (7)
O5—C7—C8	123.5 (2)	O13—Na2—O13 ^v	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 2
 Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 \cdots O15 ^{iv}	0.90	1.95	2.693 (2)	140
O5—H4 \cdots O15 ^{vi}	0.82	1.97	2.688 (2)	146
O9—H7 \cdots O4 ^{vii}	0.90	1.97	2.831 (3)	159
O9—H8 \cdots O14 ^{vii}	0.90	1.86	2.756 (3)	176
O10—H9 \cdots O4 ^{vii}	0.90	2.16	3.033 (3)	166
O10—H9 \cdots O9	0.90	2.71	3.055 (3)	104
O10—H10 \cdots O7 ^{iv}	0.90	2.06	2.939 (3)	165
O11—H11 \cdots O3 ⁱⁱⁱ	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 \cdots O9 ⁱⁱⁱ	0.90	1.93	2.787 (3)	159
O14—H17 \cdots 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 \AA and 104 $^\circ$, 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/MSK, 2001); program(s) used to solve structure: *SHELXS97* (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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