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Bis[trimethyl(tetradecyl)ammonium] 7-hydroxy-8-phenyldiazenyl-7,8-dihydronaphthalene-1,3-disulfonate 1.8-hydrate: ionic self-assembly

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Key indicators

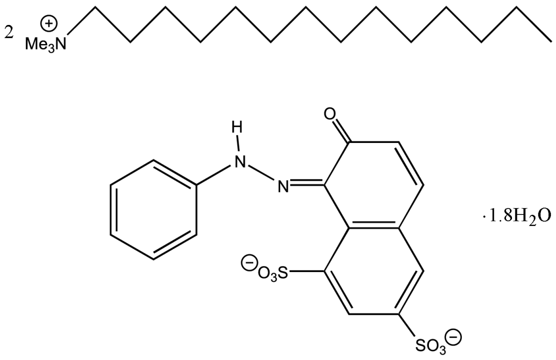
Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.006 Å
Disorder in solvent or counterion
R factor = 0.052
wR factor = 0.075
Data-to-parameter ratio = 17.4

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

Ionic self-assembly of the azobenzene dye Orange G with the surfactant tetradecylammonium bromide leads to the title compound, $2C_{17}H_{38}N^+\cdot C_{16}H_{10}N_2O_7S_2^{2-}\cdot 1.8H_2O$, which has an unusual highly regular nanostructure with ionic layers and with alternating dye and surfactant stacks.

Comment

In addition to coordination-driven self-assembly (Seidel & Stang, 2002) and hydrogen bonding (Desiraju, 2002; MacDonald & Whitesides, 1994), the use of ionic bonding (Ferlay *et al.*, 2002; Neve & Crispini, 2003; Faul & Antonietti 2003) is gaining increasing importance as a structural principle in supramolecular chemistry. The supramolecular organization of quaternary alkylammonium salts into liquid-crystalline materials has been studied extensively (Paleos, 1994). The group of Skoulios has shown that a variety of smectic mesophases can be formed by the supramolecular organization of hydroxy derivatives of quaternary alkylammonium salts (Arkas *et al.*, 1999), or, more recently, of guanidinium alkylbenzenesulfonates (Mathevet *et al.*, 2002). Recently, we have reported the formation of highly ordered self-organizing nanostructures by means of a new facile synthesis method called ionic self-assembly (ISA) (Faul & Antonietti, 2002; Guan *et al.*, 2002). This cooperative non-covalent synthesis strategy makes use of electrostatic interactions between charged surfactants and oppositely charged oligoelectrolytes. It has been shown that the nature of the tectonic units (*e.g.* azobenzene dyes exhibiting planar structures and the possibility of π–π interactions, or the number and length of the surfactant alkyl tails) plays an important role in the formation and order of the structures produced.



(I)

Some of those complexes based on azobenzene dyes (Faul & Antonietti, 2002; Guan *et al.*, 2002) form unexpectedly large crystalline and liquid-crystalline domains. It was suggested that the high molecular order observed from small-angle

X-ray scattering analyses of such self-organizing nanostructures is due to a combination of several factors: the presence of three different non-compatible sub-phases, *viz.* an alkyl sub-phase (from the surfactant tails), an ionic sub-phase (with contributions from both the surfactant as well as the oligoelectrolyte), and the oligoelectrolyte sub-phase (in the case of multiply charged azobenzene dyes, this consists of the conjugated dye backbone with distinct π-character and polarity). The large domain size is worth mentioning, as the elucidation of the structure of standard azobenzene dyes has proved to be rather difficult (Kennedy *et al.*, 2000). Their reluctance to form crystals suitable for analysis has been reported and is reflected in the small number of publications presenting such data (Anderson *et al.*, 1998; Ojala, Lu *et al.*, 1994; Ojala, Gleason *et al.*, 1994).

In this communication, we present the results of a single-crystal analysis of the ISA material $(C_{14}TA)_2OG\cdot1.8H_2O$, containing cations of the ammonium surfactant tetradecyltrimethylammonium bromide ($C_{14}TA^+Br^-$), dianions of the commercially available azobenzene dye Orange G (OG) (see scheme), and water molecules of crystallization.

The adduct crystallizes in the triclinic system, space group $P\overline{1}$. The two independent cations (Fig. 1) are both in an all-*trans* conformation. One of them (with N1) is approximately planar excluding H atoms, the maximum deviation from the least-squares plane excluding the methyl groups at N1 being 0.118 (4) Å. The second (with N2) bends in the region N2–C203 (visible in Fig. 3) leading to a maximum deviation from the mean plane of 0.743 (3) Å. The C—N bond lengths (Table 2) are between 1.478 (5) and 1.530 (4) Å. The bond lengths along the alkyl chains vary between 1.513 (5) and 1.549 (5) Å, with an average of 1.533 (5) Å.

The anion (Fig. 1) is also approximately planar [maximum deviation from the mean plane calculated for all non-H atoms except the SO_3 groups = 0.303 (3) Å]. While S2 is approximately in this plane [deviation 0.224 (1) Å], S1 is displaced from it on the opposite side by 0.798 (1) Å, with an angle of 16.9 (2)° between the S1—C1 bond and the plane. The dianion shows the hydrazone tautomeric form with a strong intramolecular N—H···O hydrogen bond, as found, for example, in the structure of the diammonium salt of Orange G (Ojala, Lu *et al.*, 1994).

The observed crystal structure (Fig. 2) is rather different from the simple three-layer structure initially envisaged. An ionic (two-dimensional) sub-phase is found in the middle of the unit cell around the (x, y, $\frac{1}{2}$) plane, thus giving a lamellar repeat period with the length of the c axis. Between these ionic layers, a non-polar two-dimensional sub-phase is situated around the (x, y, 0) planes, formed by alternating strands of the non-polar parts of the dye and the alkyl tails of surfactant cations. Contrary to simple expectations, the dye units are not arranged in extended π-stacked structures, as is usually found for calamitic structures. The reason for this might be that the π–π interactions between molecules in similar orientations are repulsive. The dye tectons, however, exhibit coplanar head-to-head arrangements in strands along the b direction (Fig. 2), with the dye backbones parallel. Water molecules are embedded between the SO_3^- groups, fixed by hydrogen bonds. One of the two independent water sites has an occupancy of only 80.3 (8)%. In layers parallel to the (102) plane, these anionic dye strands alternate with strands of surfactant ($C_{14}TA$) cations, also in a planar head-to-head arrangement (Fig. 2). By the observed tilting (~26°, Fig. 3) between the lamellar plane and the stacking vector, a favourable approximately tetrahedral coordination of both ammonium groups by four SO_3^- groups and *vice versa* is achieved, providing good local charge balance.

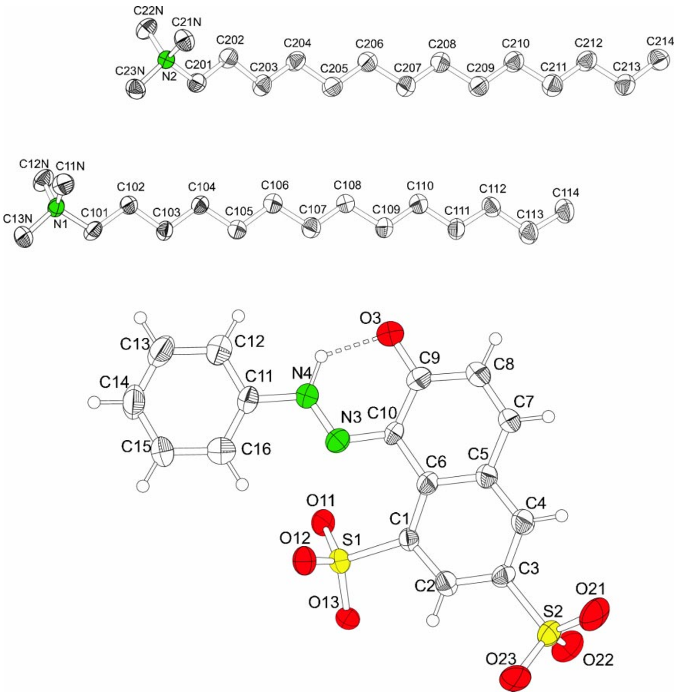


Figure 1
View (*DIAMOND*2; Crystal Impact, 2000) of the asymmetric unit (excluding water molecules) of the structure of $(C_{14}TA)_2OG$, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as small spheres of arbitrary radii.

Experimental

The title compound was synthesized by the addition of 2 equivalents of surfactant to one equivalent of OG (both 2% aqueous solutions), to yield a crystalline precipitate [see Guan *et al.* (2002) for a typical synthesis]. After centrifugation and washing, the crystals were left to stand and grow for several weeks until bright-orange thin needles of sufficient size could be isolated.

Crystal data

$2C_{17}H_{38}N^+\cdot C_{16}H_{10}N_2O_7S_2^{2-}\cdot$-1.8H$_2$O
M_r = 951.78
Triclinic, $P\overline{1}$
a = 8.2811 (14) Å
b = 13.071 (2) Å
c = 25.204 (4) Å
α = 85.82 (1)°
β = 87.96 (1)°
γ = 82.54 (1)°
V = 2696.9 (7) Å^3

Z = 2
D_x = 1.172 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7804 reflections
θ = 1.6–26.0°
μ = 0.15 mm^{-1}
T = 193 (2) K
Needle, orange
0.50 × 0.04 × 0.02 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: multi-scan (*XPREP* in *SHELXTL*; Siemens, 1996)
$T_{\min} = 0.889$, $T_{\max} = 0.997$
23 823 measured reflections
10 547 independent reflections
3416 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.106$
$\theta_{\max} = 26.2°$
$h = -9 \rightarrow 10$
$k = -16 \rightarrow 15$
$l = -31 \rightarrow 31$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.075$
$S = 0.75$
10547 reflections
605 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2)]$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.23$ e Å^{-3}
$\Delta\rho_{\min} = -0.35$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00054 (2)

Table 1
Selected geometric parameters (Å, °).

S1—O11	1.452 (2)	C3—C4	1.379 (4)
S1—O12	1.462 (3)	C4—C5	1.399 (5)
S1—O13	1.475 (2)	C5—C6	1.433 (5)
S1—C1	1.805 (3)	C5—C7	1.443 (5)
S2—O21	1.449 (3)	C6—C10	1.445 (5)
S2—O22	1.449 (3)	C7—C8	1.340 (5)
S2—O23	1.463 (3)	C8—C9	1.426 (5)
S2—C3	1.763 (4)	C9—C10	1.438 (5)
N3—N4	1.300 (4)	C11—C12	1.380 (5)
N3—C10	1.355 (4)	C11—C16	1.385 (5)
N4—C11	1.421 (4)	C12—C13	1.384 (5)
O3—C9	1.283 (4)	C13—C14	1.383 (5)
C1—C2	1.388 (5)	C14—C15	1.374 (6)
C1—C6	1.435 (4)	C15—C16	1.404 (5)
C2—C3	1.403 (5)		
O11—S1—O12	115.43 (16)	C4—C5—C6	122.0 (3)
O11—S1—O13	111.83 (15)	C4—C5—C7	118.5 (3)
O12—S1—O13	111.36 (15)	C6—C5—C7	119.5 (4)
O11—S1—C1	105.85 (15)	C5—C6—C1	116.0 (3)
O12—S1—C1	107.17 (16)	C5—C6—C10	117.2 (3)
O13—S1—C1	104.31 (16)	C1—C6—C10	126.7 (3)
O21—S2—O22	113.11 (19)	C8—C7—C5	122.5 (4)
O21—S2—O23	114.52 (19)	C7—C8—C9	120.4 (4)
O22—S2—O23	111.84 (18)	O3—C9—C8	119.0 (4)
O21—S2—C3	105.42 (18)	O3—C9—C10	121.9 (3)
O22—S2—C3	105.90 (18)	C8—C9—C10	119.1 (4)
O23—S2—C3	105.08 (18)	N3—C10—C9	122.4 (3)
N4—N3—C10	116.4 (3)	N3—C10—C6	116.4 (3)
N3—N4—C11	119.9 (3)	C9—C10—C6	120.9 (3)
C2—C1—C6	119.7 (3)	C12—C11—C16	122.3 (4)
C2—C1—S1	113.4 (3)	C12—C11—N4	115.8 (4)
C6—C1—S1	126.8 (3)	C16—C11—N4	121.8 (4)
C1—C2—C3	123.1 (3)	C11—C12—C13	118.6 (4)
C4—C3—C2	118.0 (3)	C14—C13—C12	119.7 (4)
C4—C3—S2	120.7 (3)	C15—C14—C13	122.0 (4)
C2—C3—S2	121.3 (3)	C14—C15—C16	118.8 (4)
C3—C4—C5	120.8 (3)	C11—C16—C15	118.6 (4)

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

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
N4—H4$\cdots$O3	1.007 (10)	1.73 (3)	2.480 (4)	128 (3)

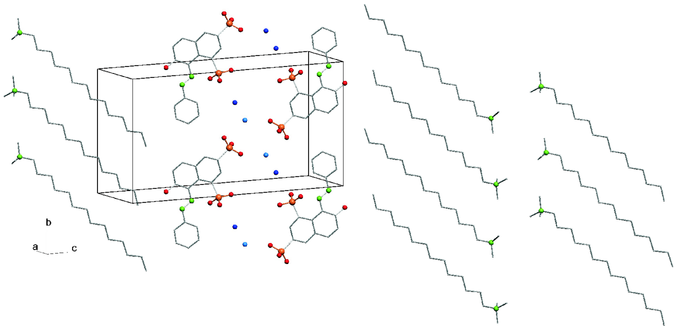


Figure 2
Arrangement of dye and surfactant ions in planes parallel to (102). Isolated spheres are water O atoms.

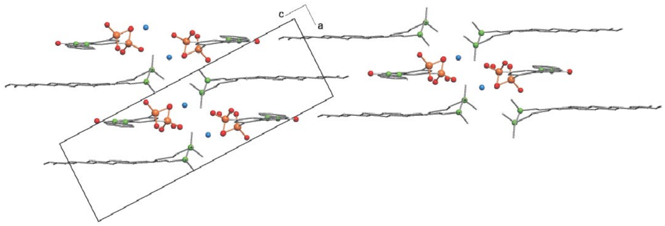


Figure 3
View along the *b* axis, in the planes shown in Fig. 2. [Reproduced with permission from Faul & Antonietti (2003)].

Refinement of the site-occupation factors for the water molecules gave 0.803 (8) for O1. It would be possible for the crystal to lose this water over a period of time without being destroyed. This observed value may therefore be specific to this crystal and thermogravimetric analysis of a powder sample might provide a different result. However, it is not thought that this would affect the final structure. H atoms bonded to C were made to ride in idealized positions (C—H = 0.95 Å in aromatic rings, 0.98 Å for CH_3 groups and 0.99 Å for CH_2 groups), with displacement parameters set at $1.2U_{\rm eq}$ (or $1.5U_{\rm eq}$ for CH_3 groups) of their parent atoms. The H atoms of the water molecules and that at N4, involved in a strong hydrogen bond, were located in a difference map, and were refined with isotropic displacement parameters common by groups for the water molecules, with geometric restraints of 0.90 (1) Å for the O—H distances, 1.46 (1) Å for the H$\cdots$H distances, and 1.00 (1) Å for the N4—H4 distance. As only very thin needles could be obtained, the data set is of low quality (number of observed reflections 32% only).

Data collection: *X-AREA WinExpose* (Stoe & Cie, 2002); cell refinement: *X-AREA WinCell* (Stoe & Cie, 2002); data reduction: *X-AREA WinIntegrate* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND*2 (Crystal Impact, 2000).

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