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Key indicators

Single-crystal X-ray study

$T = 298$ K

Mean $\sigma(\text{C}-\text{C}) = 0.006$ Å

R factor = 0.040

wR factor = 0.153

Data-to-parameter ratio = 15.5

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

Polymeric anhydrous sodium 2-amino- benzenesulfonate

The crystal structure of anhydrous sodium 2-aminobenzenesulfonate, $[\text{Na}(\text{C}_6\text{H}_6\text{NO}_3\text{S})]_n$, reveals the presence of a two-dimensional sandwich polymer structure based on a distorted octahedral six-coordinate NaO_5N repeating unit. O-Donor atoms are from five different sulfonate groups [$\text{Na}-\text{O} = 2.294(3)-2.532(3)$ Å] and an amine nitrogen [$\text{Na}-\text{N} = 2.572(3)$ Å], completing a six-membered chelate ring including Na. Hydrogen bonds also stabilize the core structure. The outer layers of the sandwich comprise the unassociated benzene rings.

Comment

Traditionally, structures of sodium salts of carboxylic acids and sulfonic acids were determined with a view to obtaining structural information about the organic component rather than considering the aspects of sodium coordination itself, *e.g.* sodium (+)-tartrate dihydrate (Ambady & Kartha, 1968). Such structures are considered to be at the upper end of the scale of Na coordination complexity, ranging from discrete molecular solvates to extensive arrays and networks (Fenton, 1986). However, irrespective of structure type, because sodium has relatively good affinity for oxygen, the coordination about the metal centres is usually quite regular, with stereochemistry similar to transition metal complexes, *e.g.* the common $\text{Na}-\text{O}_6$ octahedral (or distorted octahedral) six-coordination found in the structures of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (Ruben *et al.*, 1961; Levy & Lisensky, 1978) and $\text{NaClO}_4 \cdot 3(\text{dioxane})$ (Barnes & Weakley, 1978) is also found in sodium hydrogen (+)-tartrate (Bott *et al.*, 1994). As with the transition metal complexes, the metal stereochemistry is often forced by the constraints of the ligand, *e.g.* in sodium hydrogen (*o*-phenylenedioxy)diacetate (Bott *et al.*, 1992) it is pentagonal pyramidal, while in hydrated compounds the presence of bonded water usually results in expansion of the coordination polyhedron; the hydrates sodium hydrogen (+)-tartrate monohydrate (Bott *et al.*, 1993) and hydrated sodium *o*-phenylenedioxydiacetate (Kennard *et al.*, 1988) both have a coordination number (C.N.) of 8, while the C.N. of 5 in the unhydrated sodium 8-hydroxyquinoline-5-sulfonate (Raj *et al.*, 2002) increases to 6 in sodium 8-hydroxyquinoline-5-sulfonate trihydrate (Viossat *et al.*, 1982). This phenomenon is particularly marked when the water molecules act as space fillers in structures where sodium is a counter-ion in mixed-metal structures.

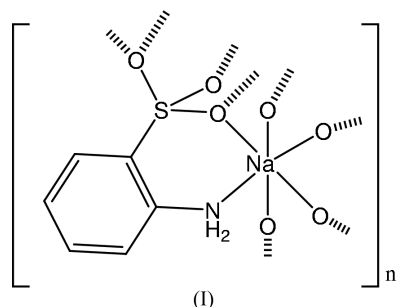
2-Aminobenzenesulfonic acid (orphanilic acid) may act as an *N,O*-bidentate chelating ligand and also has potential for polymer extension through the other O-atom donors of the flexible sulfonate group. Both of these features are exemplified in the structures of anhydrous sodium 8-hydroxyquinoline-5-sulfonate (Raj *et al.*, 2002) and its trihydrate

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(Viossat *et al.*, 1982), where uncoordinated water of solvation is also found. Other known polymeric structures of hydrated sodium salts of aromatic sulfonates are sodium sulfosalicylate dihydrate (Aliev & Atovmyan, 2001; Marzotto *et al.*, 2001) and sodium 4-hydroxybenzenesulfonate 2.4-hydrate (Kosnic *et al.*, 2002).



The structure reported here, anhydrous sodium 2-aminobenzenesulfonate, (I), demonstrates the coordination features previously described. The distorted octahedral NaO_5N coordination polyhedron comprises bonds from five O atoms of different sulfonate groups (all symmetry equivalent; two of the O atoms are bridging) [$\text{Na}-\text{O} = 2.294(3)\text{--}2.532(3)\text{ \AA}$] and one amine nitrogen [$\text{Na}-\text{N} = 2.572(3)\text{ \AA}$]. This nitrogen and one of the sulfonate O atoms [$\text{O}3^{\text{ii}}$; symmetry code: (ii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$] complete a six-membered chelate ring, similar to that found in the sodium 8-hydroxyquinoline-5-sulfonate structures (Raj *et al.*, 2002; Viossat *et al.*, 1982). The maximum deviation from the ideal $90/180^\circ$ in the bond angles about Na is $20.8(1)^\circ$ (Table 1). The result is a basic sheet polymer structure (Fig. 1), which propagates in the (100) plane (Figs. 2 and 3). The unassociated benzene rings of the acid

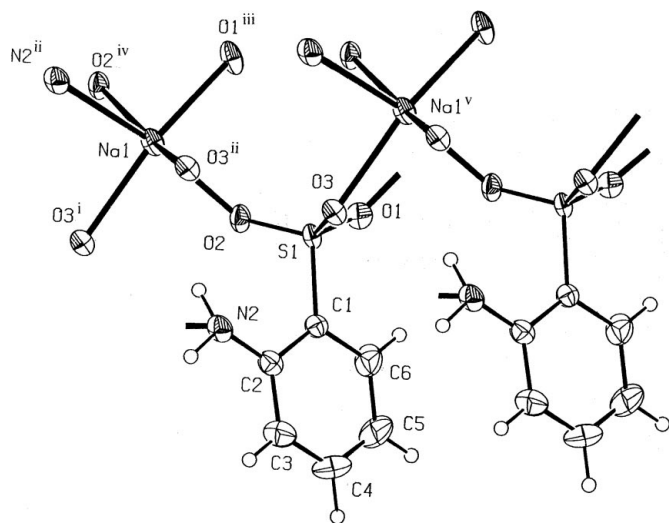


Figure 1
The molecular configuration and atom-naming scheme for the ligand molecule and the coordination polyhedron about Na in (I). Non-H atoms are drawn as 40% probability ellipsoids. The symmetry codes are as in Table 1; additionally, (v) $x, y - 1, z$.

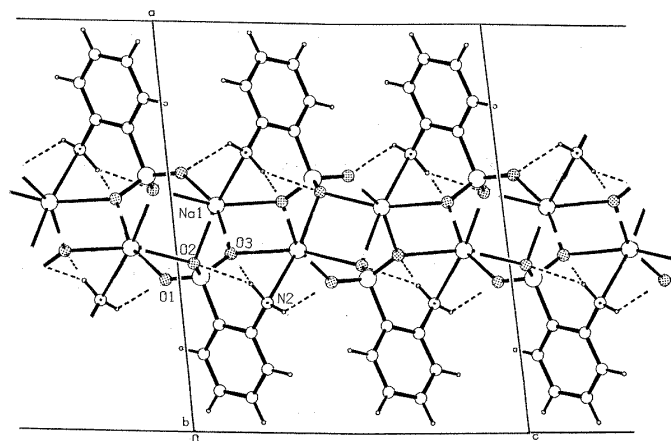


Figure 2
A layer in the structure of (I) in the unit cell, viewed down b , showing hydrogen bonds as broken lines.

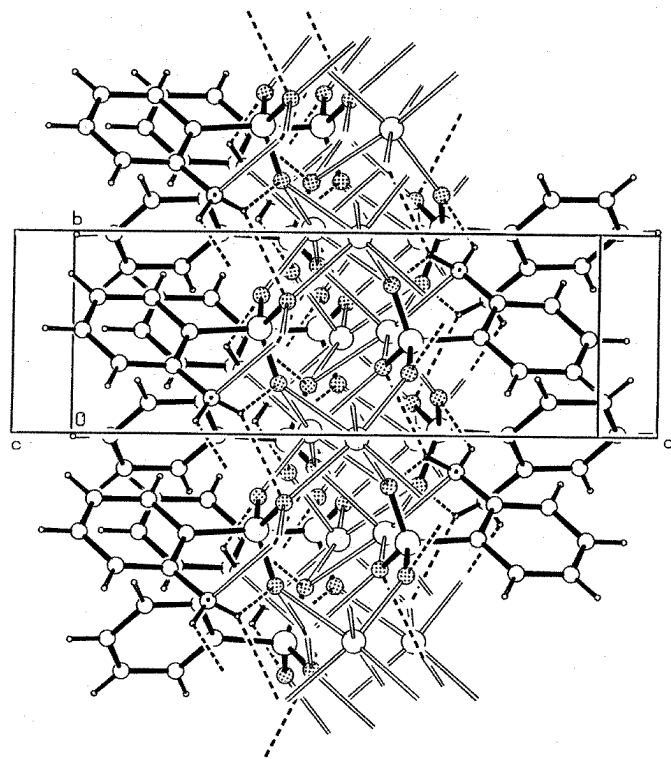


Figure 3
The packing of (I) in the unit cell, viewed down the a direction, showing the sandwich structure, with $\text{Na}-\text{O}$ bonds drawn as open lines and O atoms as stippled spheres.

residues comprise the outer extremities of the sandwich structure generated.

This structure is also stabilized through hydrogen-bonding interactions (Table 2) involving H atoms of the amino substituent, both intrasheet [$\text{N}2-\text{H}2\text{B}\cdots\text{O}1^{\text{iv}}$; $\text{N}\cdots\text{O} = 2.942(3)\text{ \AA}$; symmetry code: (iv) $x, \frac{1}{2} - y, \frac{1}{2} + z$] and intersheet [$\text{N}2-\text{H}2\text{A}\cdots\text{O}3^{\text{i}}$; $\text{N}\cdots\text{O} = 3.308(4)\text{ \AA}$; symmetry code: (i) $x, 1 + y, z$]. An intramolecular amine-sulfonate hydrogen bond is also present [$\text{N}2-\text{H}2\text{A}\cdots\text{O}2$; $\text{N}\cdots\text{O} = 2.901(3)\text{ \AA}$]. An acute $\text{C}-\text{H}\cdots\text{O}$ bond may help to maintain approximate coplanarity of the benzene ring and the $\text{S}1-\text{O}1$ bond.

Experimental

Compound (I) was isolated from the attempted synthesis of *o*-ureidobenzenesulfonate using the procedure of Davis & Blanchard (1929). This involved the reaction of 26.6 mmol of 2-aminobenzenesulfonic acid (orphanic acid) with 26.6 mmol of aqueous sodium carbonate solution (30 ml), followed by the addition of 26.6 mmol of nitroreua. After the vigorous initial reaction, the solution was boiled for 30 min, then filtered and allowed to evaporate to near dryness at room temperature, giving colourless prismatic crystals of (I) as the sole reaction product. One of these crystals was cut to provide the experimental sample.

Crystal data

[Na(C₆H₆NO₃S)]
M_r = 195.17
 Monoclinic, *P*₂₁/*c*
a = 14.213 (4) Å
b = 4.9447 (12) Å
c = 11.401 (2) Å
 β = 97.284 (19)°
V = 794.8 (3) Å³
Z = 4

D_x = 1.631 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 12.7–17.2°
 μ = 0.42 mm⁻¹
T = 298 (2) K
 Cut plate, colourless
 0.45 × 0.30 × 0.10 mm

Data collection

Rigaku AFC-7R diffractometer
 ω -2 θ scans
 Absorption correction: ψ scan
 (TEXSAN for Windows;
 Molecular Structure
 Corporation, 1999)
*T*_{min} = 0.859, *T*_{max} = 0.959
 2137 measured reflections
 1834 independent reflections

1432 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.029
 θ _{max} = 27.5°
h = -7 → 18
k = -6 → 2
l = -14 → 14
 3 standard reflections
 every 150 reflections
 intensity decay: 5.9%

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.040
wR (*F*²) = 0.153
S = 0.89
 1834 reflections
 118 parameters
 H atoms treated by a mixture of
 independent and constrained
 refinement

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 1.9146P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.011$
 $\Delta\rho_{\max} = 0.38 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.58 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Na1—O2	2.532 (3)	Na1—N2 ⁱⁱ	2.572 (3)
Na1—O3 ⁱ	2.384 (2)	Na1—O1 ⁱⁱⁱ	2.294 (3)
Na1—O3 ⁱⁱ	2.434 (2)	Na1—O2 ^{iv}	2.503 (3)
O2—Na1—O3 ⁱ	81.78 (8)	O2 ^{iv} —Na1—O3 ⁱ	92.38 (8)
O2—Na1—O3 ⁱⁱ	97.25 (8)	O3 ⁱⁱ —Na1—N2 ⁱⁱ	78.66 (8)
O2—Na1—N2 ⁱⁱ	171.54 (10)	O1 ⁱⁱⁱ —Na1—O3 ⁱⁱ	101.37 (8)
O1 ⁱⁱⁱ —Na1—O2	82.17 (9)	O2 ^{iv} —Na1—O3 ⁱⁱ	162.42 (9)
O2—Na1—O2 ^{iv}	99.92 (8)	O1 ⁱⁱⁱ —Na1—N2 ⁱⁱ	105.82 (10)
O3 ⁱ —Na1—O3 ⁱⁱ	93.78 (8)	O2 ^{iv} —Na1—N2 ⁱⁱ	84.79 (8)
O3 ⁱ —Na1—N2 ⁱⁱ	91.06 (9)	O1 ⁱⁱⁱ —Na1—O2 ^{iv}	77.40 (8)
O1 ⁱⁱⁱ —Na1—O3 ⁱ	159.15 (10)		

Symmetry codes: (i) *x*, 1 + *y*, *z*; (ii) 1 - *x*, ½ + *y*, ½ - *z*; (iii) 1 - *x*, -*y*, -*z*; (iv) 1 - *x*, 1 - *y*, -*z*.

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
N2—H2A···O2	0.94 (4)	2.22 (4)	2.901 (3)	129 (4)
N2—H2A···O3 ⁱ	0.94 (4)	2.52 (4)	3.308 (4)	142 (4)
N2—H2B···O1 ^v	0.85 (5)	2.30 (5)	2.942 (3)	132 (4)
C6—H6···O1	0.97	2.47	2.871 (5)	105

Symmetry codes: (i) *x*, 1 + *y*, *z*; (v) *x*, ½ - *y*, ½ + *z*.

All H atoms, except those on the amine substituent group of the benzenesulfonate, were included in the refinement at calculated positions (C—H = 0.95 Å) as riding atoms, with *U*_{eq} fixed at 1.2*U*_{eq}(parent atom). The amine H atoms were located by difference methods and their positional and isotropic displacement parameters were refined.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1999); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON for Windows* (Spek, 1999); software used to prepare material for publication: *PLATON for Windows*.

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