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Polymeric sodium 3,5-dicarboxybenzenesulfonate–urea–water (1/1/1)

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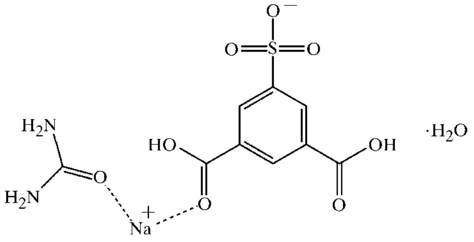
In the title compound, poly[sodium-μ_4-3,5-dicarboxybenzenesulfonato-κ^4O:O':O'':O'''-μ_2-urea-κ^2O:N] monohydrate], $\{[Na(C_8H_5O_7S)(CH_4N_2O)]\cdot H_2O\}_n$, the organic anions are arranged almost vertically within (001) monolayers, with the sulfonate and carboxylic acid groups pointing into the interlayer region. The inversion-related aromatic rings of the anions inside the layers are arrayed *via* offset face-to-face interactions into molecular stacks along the crystallographic *a* axis. The 'up' and 'down' arrangement of the aromatic portions makes both faces of the layers ionic and hydrophilic, whereas the interiors of the layers are primarily hydrophobic. The interleaving of the anions is such that the carboxylic acid groups are oriented more toward the interior than are the sulfonate groups. The aromatic rings in neighbouring layers are arranged in a herring-bone fashion. The coordination sphere of the Na^+ ions contains two sulfonate and two carboxylic acid O atoms, from a total of four different acid anions belonging to two neighbouring anionic monolayers. The urea molecules are positioned between translation-related anionic stacks inside the (001) layers, serving a triple function, *viz.* they fill in the large meshes (empty cavities) formed within the anionic–cationic network, and they provide additional Na^+ coordination and hydrogen-bond sites.

Comment

Mixed organic–inorganic compounds with layered structures have been studied intensively due to their potential chemical applications. In particular, metal phosphonates forming rigid covalent inorganic layers separated by weakly interacting organic domains are of longstanding interest, due to the possibility of manipulating the size and hydrophobic nature of the interlayer region and, therefore, the physical properties of the material (Zhang & Clearfield, 1991). More recently, metal organosulfonates have been studied as structural analogues of metal phosphonates (Gunderman & Squattrito, 1994, 1995). On the other hand, Ward and co-workers synthesized and studied numerous guanidinium alkene- and arenesulfonates displaying broad structural diversity, starting from layered materials (Russell *et al.*, 1994), and moving on to nanoporous molecular sandwiches (Russell *et al.*, 1997) and crystalline clathrates (Evans *et al.*, 1999; Holman & Ward, 2000). In an earlier paper, we studied the competition of sulfonic and carboxylic acid groups for hydrogen-bond formation and, therefore, for crystal network organization (Videnova-Adrabińska *et al.*, 2001). Here, we discuss the competitive coordination capabilities of these two groups *versus* the Na^+ ion in the title urea–sodium sulfoisophthalate (1:1) cocrystal, (I).



(I)

The coordination geometry of the Na^+ ion in (I) is sixfold and irregular, with five Na—O distances in the range 2.3065 (9)–2.4465 (9) Å. The sixth, somewhat elongated, coordination bond [Na—N2^{iv} = 2.7869 (12) Å; symmetry code: (iv) $1 - x, -y, 1 - z$] is to one of the N atoms of another urea molecule (Table 1 and Fig. 1).

A more detailed analysis of the molecular organization in the crystal of (I) reveals a helical arrangement of the ligands

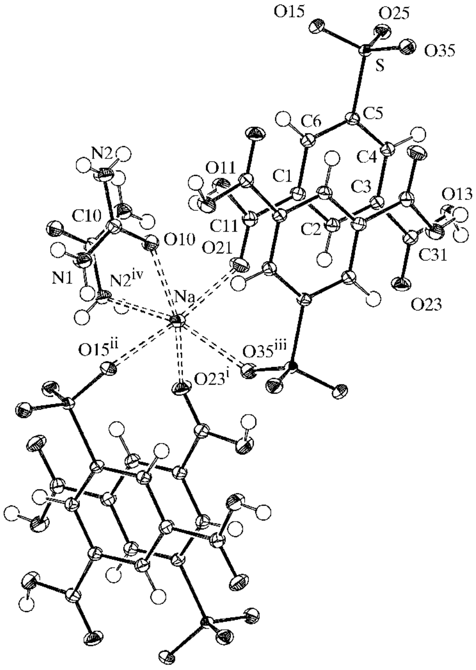


Figure 1
A view of the coordination sphere around the Na^+ ion in (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii (symmetry codes are as given in Table 1).

around the Na^+ ions (Fig. 2). Only the carboxylic acid groups are involved in the formation of the helical chains that run up and down along the crystallographic *b* direction [Na—O21 = 2.3223 (9) Å and Na—O23^i = 2.3065 (9) Å; symmetry code: (i) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$]. On the other hand, the sulfonate group, providing two additional O-atom coordination sites, serves to associate neighbouring helical chains into double helices [Na—O35^{iii} = 2.4230 (9) Å and Na—O15^{ii} = 2.4465 (9) Å; symmetry codes: (ii) $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$; (iii) $1-x, 1-y, 1-z$].

The three-dimensional crystal network of (I) is furnished by dense packing of these double helices *via* translation relations in the *a* and *c* directions, so that the overall crystal architecture can be considered as consisting of (001) organic layers with alternating sulfoisophthalate and urea galleries (Fig. 3). The aromatic rings located in the turns of the helices are alternately arranged in (210) and ($\bar{2}10$) planes in order to form stacks along the *a* axes, with consecutive offset face-to-face and van der Waals interactions in between. The urea molecules are embedded in the anionic–cationic network so as to occupy the empty filaments (corridors) generated between the sulfoisophthalate galleries. The narrow inorganic regions, where the Na^+ ions reside, link the organic monolayers.

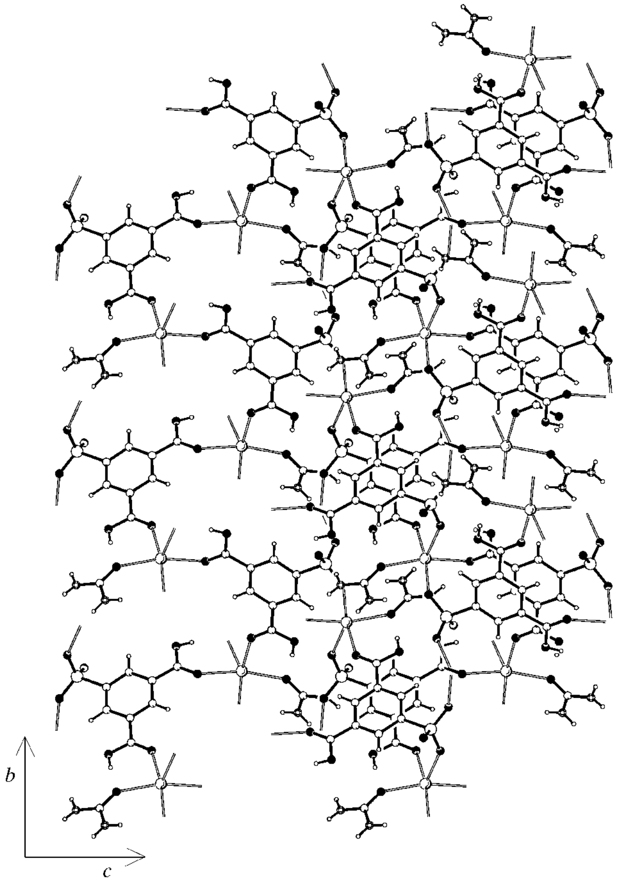


Figure 2
Views of the single helical chain running along the *b* direction (left) and of the double helix (right), which is formed by two inversion-related chains ('up' and 'down' strands) and translated along the *c* axis relative to the single chain.

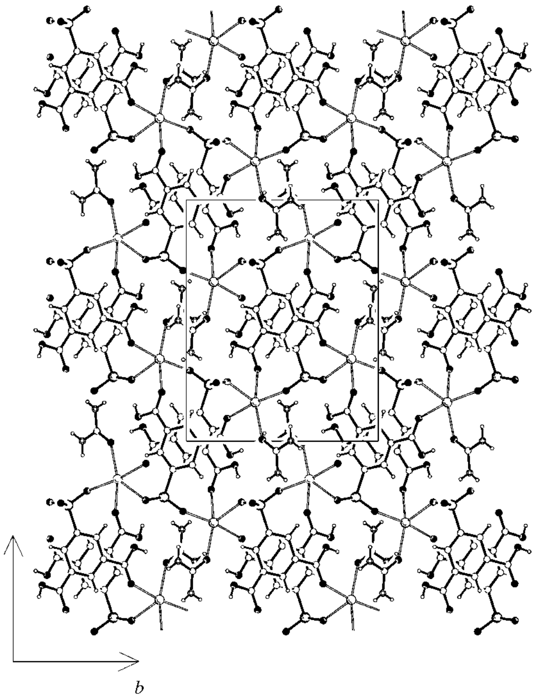


Figure 3
A view of the crystal structure of (I) along the *a* axis, showing the coordination network. The urea and sulfonic acid moieties are stacked in galleries along the *a* axis and form undulating (001) organic layers that are separated by narrow inorganic regions. Both faces of the layers are ionic and hydrophilic, whereas the interior of the layer is divided into hydrophobic and hydrophilic filaments (Fig. 4). For the sake of clarity, water molecules and hydrogen bonds have been omitted.

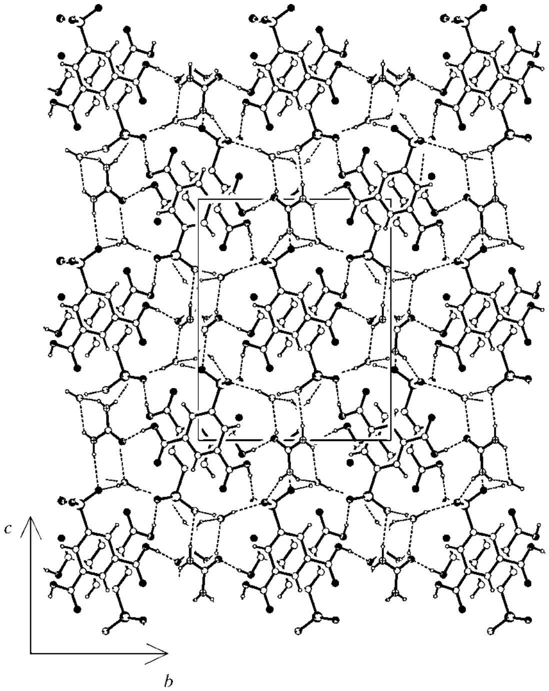


Figure 4
The same view as in Fig. 3, but showing the three-dimensional hydrogen-bonded network in (I) (coordination bonds have been omitted). The urea molecules, *via* a strong hydrogen bond donated from one of the carboxylic acid groups, serve to link the hydrophobic filaments in the layers. Carboxylic acid–sulfonate, urea–water and water–sulfonate hydrogen bonds interweave the monolayers.

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Numerous hydrogen bonds to and from the urea and water molecules additionally stabilize the three-dimensional architecture of (I) (Table 2 and Fig. 4). A relatively short hydrogen bond [O11—H1$\cdots$O10 = 2.5495 (11) Å] is formed between the sulfoisophthalate and the urea ligands inside the monolayers. Another hydrogen bond, formed between one of the carboxylic acid groups and the sulfonate group of a reflection-related anion [O13—H3$\cdots$O35^{i} = 2.7052 (11) Å], traverses the interlayer region along the [10$\overline{1}$] direction, in addition to the coordination bonds. A non-coordinated crystal water molecule also stabilizes the three-dimensional crystal architecture *via* four hydrogen bonds (Table 2).

In conclusion, it is pertinent to draw attention to the coordination properties of the Na$^+$ ion. Although the sulfonic acid group is deprotonated, the Na$^+$ cation is distributed between both the carboxylic acid groups and the sulfonate group. Therefore, the anion–cation interrelations are changed from purely ionic interactions to coordination bonds. Interestingly, the non-charged carboxylic acid groups coordinate to the Na$^+$ ion more strongly than the formally charged sulfonate group.

Experimental

The synthesis of (I) was carried out by the reaction of sodium 5-sulfoisophthalate (0.50 g) and urea (0.22 g) dissolved in a hot mixture of H_2O and methanol (10 ml, 1:1). The reaction solution was allowed to stand at room temperature for 12 d, whereupon colourless crystals of (I) were obtained. Prior to the X-ray measurements, the crystal sample was polished with the aid of water in order to obtain a spherical shape.

Crystal data

$[Na(C_8H_5O_7S)(CH_4N_2O)]\cdot H_2O$
M_r = 346.26
Monoclinic, $P2_1/n$
a = 8.203 (3) Å
b = 11.566 (4) Å
c = 14.534 (4) Å
β = 91.025 (3)°
V = 1378.7 (8) Å^3
Z = 4
D_x = 1.668 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 15 999 reflections
θ = 2–37°
μ = 0.32 mm^{-1}
T = 100 K
Spherical, colourless
0.3 × 0.3 × 0.3 mm

Data collection

Kuma KM-4 CCD area-detector diffractometer
ω scans
22 990 measured reflections
6900 independent reflections
5744 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.024
$\theta_{\rm max}$ = 37.5°
$h = -14 \rightarrow 12$
$k = -19 \rightarrow 19$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.091
S = 1.10
6900 reflections
244 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0469P)^2 + 0.1356P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.001
$\Delta\rho_{\rm max}$ = 0.57 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.50 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0033 (9)

Refined C—H distances are in the range 0.910 (4)–0.973 (15) Å.

Data collection: *KM*-4 *CCD Software* (Kuma, 1995–1999); cell refinement: *KM*-4 *CCD Software*; data reduction: *KM*-4 *CCD Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003).

Table 1
Selected geometric parameters (Å, °).

Na—O21	2.3223 (9)	Na—O35^{iii}	2.4230 (9)
Na—O23^{i}	2.3065 (9)	Na—O10	2.3362 (9)
Na—O15^{ii}	2.4465 (9)	Na—N2^{iv}	2.7869 (12)
O21—Na—O15^{ii}	171.69 (3)	O35^{iii}—Na—O15^{ii}	94.88 (4)
O21—Na—O35^{iii}	88.31 (4)	O35^{iii}—Na—N2^{iv}	155.14 (3)
O21—Na—O10	81.98 (3)	O10—Na—O15^{ii}	89.79 (3)
O21—Na—N2^{iv}	93.44 (4)	O10—Na—O35^{iii}	119.79 (3)
O23^{i}—Na—O21	98.46 (3)	O10—Na—N2^{iv}	84.96 (3)
O23^{i}—Na—O15^{ii}	89.63 (3)	C10—O10—Na	139.33 (6)
O23^{i}—Na—O35^{iii}	80.69 (3)	Na^{iv}—N2—H1N2	92.2 (12)
O23^{i}—Na—O10	159.48 (3)	Na^{iv}—N2—H2N2	90.0 (10)
O23^{i}—Na—N2^{iv}	74.52 (3)	C10—N2—Na^{iv}	105.62 (6)
O15^{ii}—Na—N2^{iv}	86.88 (4)		

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O11—H1$\cdots$O10	0.841 (19)	1.714 (19)	2.5495 (11)	171.9 (19)
O13—H3$\cdots$O35^{i}	0.84 (2)	1.87 (2)	2.7052 (11)	173 (2)
N1—H1N1$\cdots$O15^{ii}	0.862 (17)	2.275 (17)	3.0881 (13)	157.3 (14)
N1—H2N1$\cdots$O1W^{iii}	0.869 (16)	2.282 (17)	2.9974 (13)	139.6 (14)
N2—H1N2$\cdots$O25^{iv}	0.783 (17)	2.192 (17)	2.9463 (12)	161.8 (16)
N2—H2N2$\cdots$O1W^{iii}	0.826 (14)	2.142 (14)	2.8984 (14)	152.1 (13)
O1W—H1$W\cdots$O25^{iv}	0.85 (2)	2.00 (2)	2.8252 (13)	165.5 (17)
O1W—H2$W\cdots$O15	0.79 (2)	2.17 (2)	2.9461 (13)	171.1 (19)

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

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