crystalline state at room temperature and at 77°K. To explain the dissipation of the absorbed energy, an efficient radiationless deactivation process was sought, such as aggregation in solution. No evidence of aggregation could be found in the molecular weight determination. For this reason the structure determination of HMB and of HMCB which shows the presence of dimers of centrosymmetrically related molecules is an important new element in the understanding of the photostability of these hydroxy derivatives of benzophenone.

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Crystal Structures of Acid Hydrates and Oxonium Salts. IX. *o*-Sulphobenzoic Acid Trihydrate*

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The structure of $C_6H_4(COOH)SO_3H.3H_2O$ has been determined from 3180 X-ray intensities collected on an automatic diffractometer, and refined, including H atoms, to $R=0{\cdot}038$. The crystals are triclinic, space group $P\bar{1}$, with $a=6{\cdot}954$ (1), $b=11{\cdot}741$ (2), $c=7{\cdot}872$ (1) Å, $\alpha=102{\cdot}11$ (1), $\beta=111{\cdot}73$ (2), $\gamma=103{\cdot}83$ (2)°, $Z=2$. The anions, deprotonated at the sulpho group only, are stacked in layers. Successive layers are connected by the interleaving water structure, which with a short [O–O: 2·404 (2) Å] and a normal [2·714 (2) Å] hydrogen bond is $H_5O_2^+.H_2O$. There is no hydrogen bonding directly between anions.

Introduction

For investigation of higher hydrated protons in the crystalline state, the hydrates of aromatic sulphonic acids are of special interest. Mostly these hydrates contain more than one molecule of water, thus enabling the acid proton of the sulpho group to form various cationic water species. X-ray and neutron investigations show the cation $H_7O_3^+$ in the following trihydrates: 5-sulphosalicylic acid (X-ray: Mootz & Fayos, 1970; neutron: Williams & Peterson, 1972), 2,5-dichlorobenzenesulphonic acid (Lundgren & Lundin, 1972) and 2,5-dibromobenzenesulphonic acid (Lundgren, 1972*a*). The tetrahydrate of picrylsulphonic acid (X-ray: Lundgren, 1972*b*; neutron: Lundgren &

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* Part of the dissertation of R. Attig, Braunschweig, 1973. Part VIII: Attig & Mootz (1975). *Z. anorg. allgem. Chem.* In the press.

Tellgren, 1974) contains an $H_5O_2^+$ cation besides two water molecules, the latter connected in an endless chain. Also the structures of two modifications of the monohydrate of *p*-toluenesulphonic acid are known, both containing an H_3O^+ cation (Arora & Sundaralingam, 1971; Dexter, 1971). The geometry of this species was confirmed by a neutron diffraction study of the monoclinic form (Lundgren & Williams, 1973). The present work gives the structure of another trihydrate of an aromatic sulphonic acid.

Experimental

o-Sulphobenzoic acid was prepared from the commercially available ammonium salt by removing the ammonia with $Ba(OH)_2$ and then precipitating $BaSO_4$ with H_2SO_4. Slow cooling of a saturated aqueous solution revealed long square prisms of the trihydrate stable in air.

The Laue group was established by Weissenberg photographs along [100] (prism axis), [010] and [012]. Accurate setting angles of 24 strong high-order reflexions were determined on a diffractometer; a least-squares refinement yielded $a=6{\cdot}954$ (1), $b=11{\cdot}741$ (2), $c=7{\cdot}872$ (1) Å, $\alpha=102{\cdot}11$ (1), $\beta=111{\cdot}73$ (2), $\gamma=103{\cdot}83$ (2)°. With $V=544{\cdot}38$ Å^3 and $\varrho_m=1{\cdot}542$ g cm^{-3} the cell contains two (1·97) formula units. Intensities were collected on an automatic single-crystal diffractometer (Siemens AED). 3180 unique reflexions including 363 'less thans' were measured up to 30° in θ with Zr-filtered Mo $K\alpha$ radiation. Four standard reflexions measured after every 50 reflexions remained constant. No absorption correction was applied ($\mu=3{\cdot}2$ cm^{-1}).

Structure determination and refinement

The sharpened, origin-removed Patterson function showed not only the S–S vector, but also all S–C and S–O vectors of two symmetry related molecules in $P\bar{1}$. Subsequent structure factor calculation and Fourier synthesis gave the atomic positions of the three water O atoms. The parameters of all S, O, C atoms were refined isotropically (three cycles, $R=0{\cdot}108$) and anisotropically (three cycles, $R=0{\cdot}050$) by least-squares calculations, with weights derived from counting statistics. A difference synthesis was calculated with restricted data ($\sin\theta/\lambda<0{\cdot}5$ Å^{-1}). Maxima between 0·64 and 0·54 e Å^{-3} could be cor-

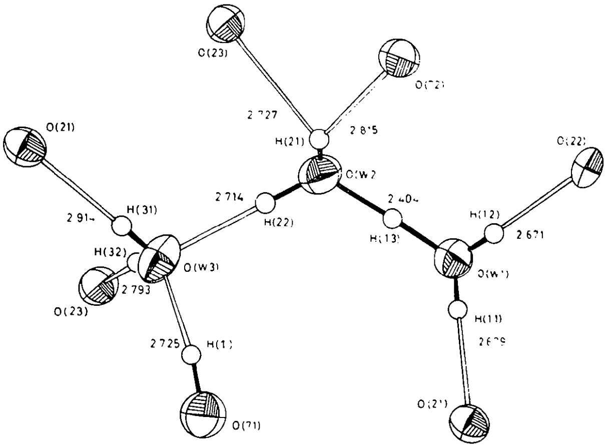

Fig. 1. The surroundings of the three water molecules showing all hydrogen bonds of the structure.

Table 1. *Atomic parameters and their standard deviations*

B values in Å^2. The B_{ij} of the heavy atoms correspond to the expression exp $[\frac{1}{4}(B_{11}h^2a^{*2}+2B_{23}klb^*c^*+\ldots)]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	0·38710 (5)	0·29234 (3)	0·44103 (4)	2·59 (1)	2·20 (1)	1·85 (1)	1·06 (1)	1·08 (1)	0·87 (1)
O(21)	0·62479 (15)	0·34787 (8)	0·56808 (13)	2·68 (5)	2·56 (5)	3·20 (5)	0·70 (4)	1·28 (4)	0·86 (4)
O(22)	0·33853 (19)	0·27499 (10)	0·23833 (13)	5·28 (6)	3·55 (5)	2·32 (5)	1·95 (5)	1·96 (5)	1·41 (4)
O(23)	0·26298 (16)	0·36055 (9)	0·50327 (13)	3·57 (5)	3·53 (5)	2·60 (4)	2·20 (4)	1·45 (4)	1·30 (4)
O(71)	0·59145 (25)	0·16983 (13)	0·95324 (17)	7·21 (9)	4·76 (7)	2·52 (5)	3·59 (7)	0·80 (6)	1·29 (5)
O(72)	0·46046 (20)	0·31065 (10)	0·85818 (14)	5·55 (7)	3·24 (5)	2·51 (5)	2·11 (5)	1·11 (5)	0·97 (4)
O(*W*1)	0·18762 (20)	0·44537 (11)	1·11636 (16)	4·86 (6)	2·99 (5)	2·69 (5)	1·41 (5)	1·30 (5)	1·02 (5)
O(*W*2)	0·16531 (20)	0·44185 (11)	0·80297 (15)	4·16 (6)	3·96 (6)	2·93 (5)	2·08 (5)	1·77 (5)	1·05 (5)
O(*W*3)	0·16802 (18)	0·64505 (11)	0·69231 (15)	3·00 (5)	5·32 (7)	2·56 (5)	1·84 (5)	1·31 (5)	1·64 (5)
C(1)	0·35353 (20)	0·11115 (11)	0·62204 (17)	2·40 (6)	2·54 (6)	2·42 (5)	1·10 (5)	1·05 (5)	1·01 (5)
C(2)	0·29855 (19)	0·13907 (11)	0·44881 (17)	2·04 (5)	2·21 (5)	2·17 (5)	0·79 (4)	0·82 (4)	0·70 (4)
C(3)	0·17830 (23)	0·04287 (13)	0·27057 (20)	3·00 (6)	2·85 (6)	2·43 (6)	0·71 (5)	0·72 (5)	0·44 (5)
C(4)	0·10758 (26)	−0·08025 (14)	0·26185 (24)	3·26 (7)	2·58 (6)	3·69 (7)	0·46 (6)	0·93 (6)	0·08 (6)
C(5)	0·16141 (25)	−0·10824 (13)	0·42872 (26)	3·14 (7)	2·22 (6)	5·02 (9)	0·77 (5)	1·54 (7)	1·10 (6)
C(6)	0·28501 (23)	−0·01389 (13)	0·60792 (23)	3·16 (7)	2·90 (6)	3·69 (7)	1·34 (6)	1·53 (6)	1·74 (6)
C(7)	0·47336 (22)	0·20889 (12)	0·82034 (18)	3·26 (6)	3·03 (6)	2·15 (5)	1·38 (5)	1·24 (5)	1·22 (6)

	x	y	z	B		x	y	z	B
H(1)	0·650 (4)	0·226 (3)	1·057 (4)	6·2 (7)	H(12)	0·250 (3)	0·400 (2)	1·160 (3)	4·2 (5)
H(3)	0·157 (3)	0·065 (2)	0·153 (3)	4·2 (5)	H(13)	0·194 (3)	0·446 (2)	0·977 (3)	7·0 (5)
H(4)	0·038 (3)	−0·149 (2)	0·146 (3)	4·4 (5)	H(21)	0·241 (5)	0·419 (3)	0·781 (4)	6·6 (8)
H(5)	0·121 (4)	−0·195 (2)	0·430 (3)	6·0 (6)	H(22)	0·166 (4)	0·511 (2)	0·760 (3)	5·5 (6)
H(6)	0·328 (3)	−0·032 (2)	0·726 (3)	3·5 (5)	H(31)	0·211 (4)	0·642 (2)	0·611 (3)	5·2 (6)
H(11)	0·258 (4)	0·512 (2)	1·216 (4)	5·4 (6)	H(32)	0·032 (4)	0·641 (2)	0·623 (3)	4·1 (5)

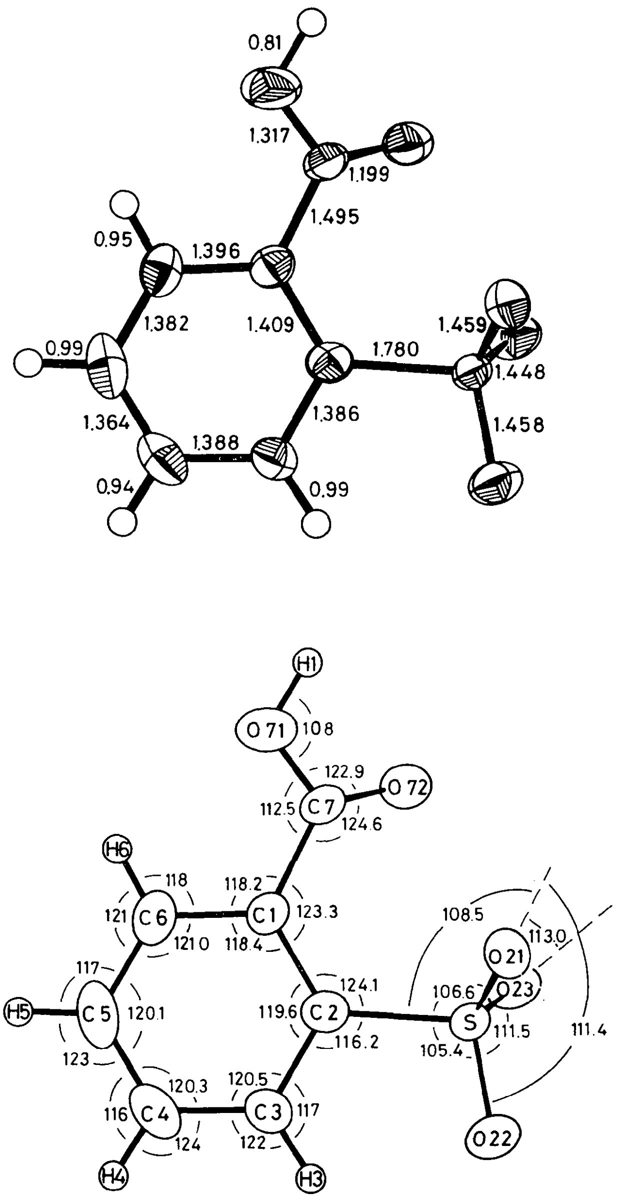

Fig. 2. The *o*-carboxybenzenesulphonate ion with distances (above; e.s.d. 0·002, from S 0·001 Å) and angles (below, with atom labelling; e.s.d. 0·1° for heavy atoms and 1–2° involving H).

related with benzene H atoms; the next highest maxima down to 0·41 e Å^{-3} gave the positions of the carboxylic and water H atoms. Several maxima below 0·34 e Å^{-3} appeared in bonds within the benzene ring and to the two substituents. Among these maxima the last H atom was found, situated in a very short O–O contact of the water structure.

A final refinement of all parameters, including the H atoms with isotropic temperature factors, gave R = 0·038 for all reflexions (0·034 for observed only) and R_w = 0·040. Atomic parameters are listed in Table 1. The atomic form factors of Hanson, Herman, Lea & Skillman (1964) were used for S, O and C, those of Stewart, Davidson & Simpson (1965) for H.*

Discussion

As expected, the structure is made up of anions deprotonated at the sulpho group only and of a cationic water structure. The environment of the three water molecules is shown in Fig. 1, hydrogen bonds are listed in Table 2. Bond lengths and angles of the anion are given in Fig. 2.

Hydrogen bonds

All hydrogen bonds of the structure engage at least one water molecule. The hydrogen bonds between the water molecules are of quite different lengths: O(W1)–O(W2) has the very short distance of 2·404 Å indicative of an $H_5O_2^+$ cation, whereas O(W2)–O(W3) at 2·714 Å approximates the hydrogen-bonding distance of ice. Therefore a reasonable structural formulation of the compound is $[H_5O_2^+ . H_2O]\,[o\text{-}C_6H_4(COOH)SO_3^-]$, diaquoproton *o*-carboxybenzenesulphonate hydrate. Owing to the unequal environment of O(W1) and O(W2) no exactly centred hydrogen bond can be expected, as several neutron diffraction studies (Williams & Peterson, 1969; Williams & Schneemeyer, 1973; Lundgren & Tellgren, 1974) show. The greater part of the excess protonic

Table 2. *Geometry of the hydrogen bonds*

Roman numerals correspond to the symmetry operations: (I) $1-x, 1-y, 2-z$; (II) $1-x, 1-y, 1-z$; (III) $x, 1-y, 1-z$.

D–H$\cdots A$	$D\cdots A$	D–H	H$\cdots A$	$\angle DHA$
O(W1)–H(11)$\cdots$O(21$^{\rm I}$)	2·679 (2) Å	0·85 (2) Å	1·83 (2) Å	172 (3)°
O(W1)–H(12)$\cdots$O(22$^{\rm II}$)	2·671 (2)	0·82 (3)	1·86 (3)	170 (2)
O(W1)–H(13)$\cdots$O(W2)	2·404 (2)	1·12 (3)	1·30 (3)	170 (2)
O(W2)–H(21)$\cdots$O(23)	2·727 (2)	0·71 (4)	2·21 (3)	132 (2)
$\cdots$O(72)	2·815 (2)		2·21 (3)	145 (2)
O(W2)–H(22)$\cdots$O(W3)	2·714 (3)	0·95 (2)	1·77 (3)	177 (2)
O(W3)–H(31)$\cdots$O(21$^{\rm II}$)	2·914 (2)	0·80 (2)	2·12 (3)	171 (2)
O(W3)–H(32)$\cdots$O(23$^{\rm III}$)	2·797 (2)	0·88 (2)	1·91 (2)	174 (2)
O(71$^{\rm I}$) –H(1$^{\rm I}$)$\cdots$O(W3)	2·725 (2)	0·81 (2)	1·92 (2)	170 (3)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31207 (13 pp. 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

charge seems to be located at O(*W*1), indicated by the shorter hydrogen bonds of this water O atom to two sulphonyl O atoms and in agreement with the refined position of H(13). O(*W*2) is engaged also in the longer contact between water molecules and in a bifurcated hydrogen bond to one sulphonyl and one carboxyl O atom; all these distances are greater than 2·7 Å. The two water molecules of the $H_5O_2^+$ cation display flat trigonal pyramids in their H and O atom environment, the two acceptors of the bifurcated bond considered in one averaged position. The conformation of this $H_5O_2^+$ cation is *cis*, slightly twisted. Contrarily, the third water molecule is engaged in four tetrahedrally arranged hydrogen bonds. This is achieved by the two hydrogen bonds donated from this water molecule to two sulphonyl O atoms, and by the bonds accepted from O(*W*2) and from the carboxylic OH group. This last hydrogen bond seems to prevent the three water molecules from forming $H_7O_3^+$, as they do in 2,5-dichloro- and 2,5-dibromobenzenesulphonic acid. $H_7O_3^+$ cations also exist in the two known modifications of 5-sulphosalicylic acid trihydrates (Mootz & Fayos, 1970; Attig & Mootz, 1974), with one more functional substituent on the benzene ring. But here the hydrogen-bond donor groups are 'saturated' in intra- and inter-molecular contacts and do not disturb the water arrangement (Attig, 1975).

In cases of higher 'concentrations' of water molecules with respect to the anionic part the arrangement of an $H_5O_2^+$ cation and a neutral water molecule in hydrogen-bonded endless chains is reported. In the trihydrates of HCl (Lundgren & Olovsson, 1967) and HBr (Lundgren, 1970) the chains run through both ends of the cations; in the hexahydrate of nitranilic acid (Andersen & Andersen, 1975; neutron study: Williams & Peterson, 1969) through one end only.

The o-carboxybenzenesulphonate ion

The anion may be compared with that in ammonium acid *o*-carboxybenzenesulphonate (Okaya, 1967). The average bond length in the benzene ring, 1·387 Å, agrees well with that of Okaya (1·384 Å), but has an increased variance. Both rings have the shortest bond opposite to the one between the *ortho* substituents. Additional distortion of the benzene ring from hexagonal regularity is significant only in the trihydrate, where the bond C(1)–C(2) is lengthened to 1·409 Å. This and the distribution of bond angles at C(1) and C(2) can be explained by stronger repulsive forces between the *ortho* substituents resulting from a smaller rotation of the carboxylic group out of the ring plane (Fig. 3). The un-ionized carboxylic group has, as usual, two unequal C–O distances and also unequal C–C–O angles. The sulphonate group agrees well with the dimensions given by Okaya. Similar S–O lengths near 1·455 Å (average) and angles near 112·0° (O–S–O) and 106·8° (C–S–O) clearly show the deprotonation of this group. The small but significant shortening of S–O(23) can be correlated with the hydrogen bonding. O(23) is engaged only in the weak hydrogen bond from the water molecule O(*W*3) and the bifurcated and also weak hydrogen bond from O(*W*2), whereas the longer bonded sulphonyl O atoms are linked to O(*W*1) by strong hydrogen bonds.

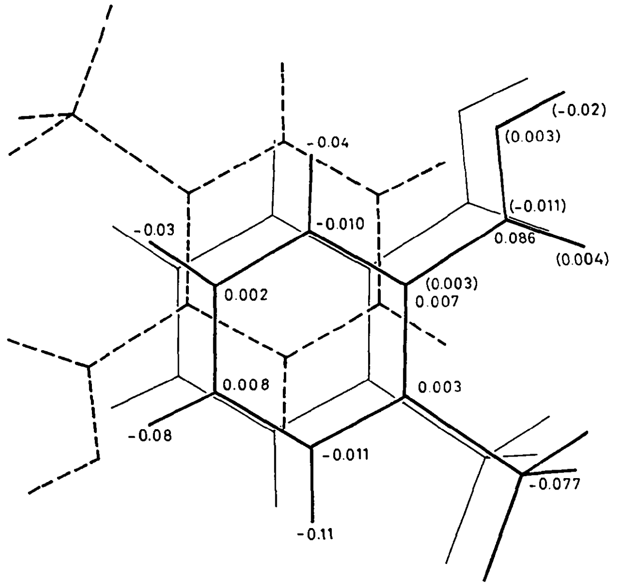

Fig. 4. Packing of benzene rings in columns. Two translationally equivalent anions are given in full lines, sandwiching an inverted one (broken lines). Deviations from the best plane through ring C atoms are given in Å for one molecule; in brackets deviations from the best plane of the carboxy group.

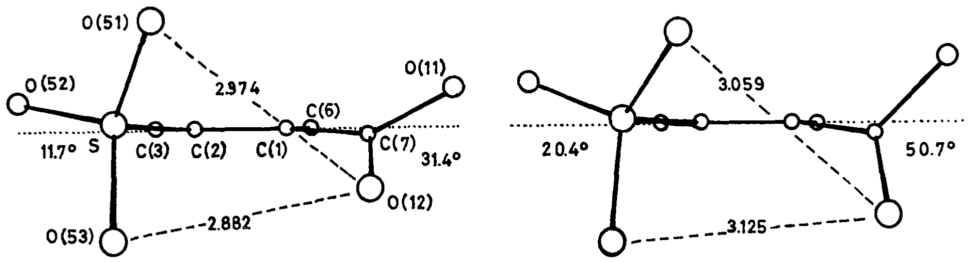

Fig. 3. Comparison of the *o*-carboxybenzenesulphonate anions of the trihydrate (left) and of the ammonium salt (right), viewed between the substituents and in the ring plane. Twist angles of the least tilted sulphonyl O and the planes of the carboxy group against the ring planes (dotted) are given. Broken lines show shortest O–O contacts in Å.

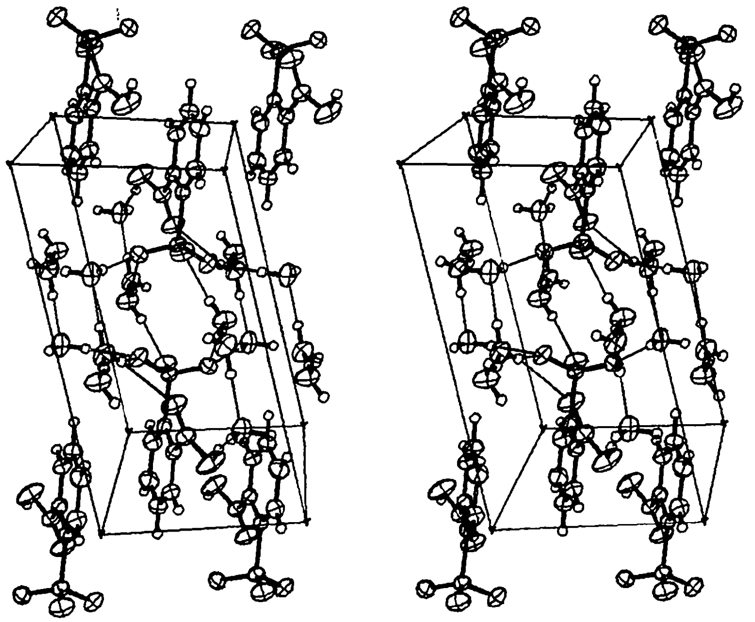

Fig. 5. Stereoscopic drawing of the crystal structure of *o*-sulphobenzoic acid trihydrate, origin in the remote lower right corner, **a** pointing to the left, **b** up and **c** forward.

Packing of cations and anions

The benzene rings are stacked to build columns along **a**. The line normal to the planes deviates from **a** by 4·3°. Fig. 4 shows two translationally equivalent anions and one inverted between them. The distances between these rings are 3·42 and 3·51 Å. The columns are packed in hydrophobic layers parallel to the *ac* plane, with the *ortho* substituents pointing outwards in opposite directions. Successive layers are connected by hydrogen bonds of the interleaving water structure (Fig. 5). Two anions, with the sulpho groups pointing to a common centre of symmetry, and their translational equivalents along **c**, make up ribbons firmly hydrogen bonded by the $H_5O_2^+$ cation, which itself is extended along **c**, and the water molecule O(*W*3). Only one hydrogen bond of this neutral water molecule connects these ribbons along [100]. There are no hydrogen bonds between the anions.

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