Acta Cryst. (1984). C**40**, 1696–1698

Dipotassium Sodium Trisaccharinate Monohydrate,* $K_2Na(C_7H_4NO_3S)_3.H_2O$

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(*Received* 26 *April* 1984; *accepted* 13 *June* 1984)

Abstract. $M_r = 665{\cdot}74$, triclinic, $P\bar{1}$, $a = 16{\cdot}428\,(5)$, $b = 12{\cdot}122\,(4)$, $c = 6{\cdot}954\,(1)$ Å, $\alpha = 97{\cdot}61\,(2)$, $\beta = 77{\cdot}36\,(2)$, $\gamma = 110{\cdot}09\,(2)°$, $V = 1266{\cdot}52$ Å^3, $Z = 2$, D_m(flotation) = 1·72, $D_x = 1{\cdot}74$ g cm^{-3}, μ(Mo $K\alpha$) = 6·3 cm^{-1}, $\lambda = 0{\cdot}71069$ Å, $F(000) = 676$, $T = 294$ K, final $R = 0{\cdot}054$ for 4724 reflections with $F_o > 3\sigma(F_o)$. The structure consists of one Na^+ and two independent K^+ cations, three independent $C_7H_4NO_3S^-$ anions and one H_2O molecule, in a polymeric framework. The anions are bonded to the cations through the N as well as the carbonyl and sulphonyl O atoms. The H_2O molecule forms bridges between two Na^+ and between one Na^+ and one K^+ ion, and is also involved in H bonds with the carbonyl groups of two $C_7H_4NO_3S^-$ anions.

Introduction. Very little was known about the chemistry of metal–saccharin (*o*-sulphobenzoimide) compounds before we reported the first structural characterization of the Cu^{II} complex, $[Cu(C_7H_4NO_3S)_2(H_2O)_4].2H_2O$ (Ahmed, Habib, Haider, Malik & Hursthouse, 1981). The structures of the corresponding Mn^{II} (Kamenar & Jovanovski, 1982), Fe^{II}, Co^{II}, Ni^{II} (Haider, Malik, Ahmed, Hess, Riffel & Hursthouse, 1983), Zn^{II} and Cd^{II} (Haider, Malik, Das & Hursthouse, 1984) have now been described. We have further shown that saccharin reacts rather easily with Ag^I, Pd^{II}, Hg^{II}, Tl^I and Pb^{II} to produce a variety of compounds, some of which have been structurally characterized (Malik, Haider, Hursthouse & Wadsten, 1984). The importance of these new compounds lies in the potential use of saccharin as an antidote for metal poisoning. As a natural extension of this work, we have also sought to examine in detail the nature of compounds that may be formed with alkali and alkaline-earth metals, and so far we have prepared a number of compounds with Na^I, K^I, Mg^{II}, Ca^{II}, Sr^{II} and Ba^{II}. The details of the preparation and properties of these materials will be published elsewhere. In the present paper, we describe the structure determination of the title compound which contains both Na^I and K^I ions. The structures of two related compounds, $Na_3(C_7H_4NO_3S)_3.2H_2O$ and $Mg(C_7H_4NO_3S)_2.7H_2O$, have recently been reported (Jovanovski & Kamenar, 1982).

Experimental. Preparation by reacting the commercially available Na salt of saccharin $[Na(C_7H_4NO_3S).2H_2O]$ with KCl in aqueous medium. Bundles of colourless, very long needles which initially formed were unsuitable for X-ray work; some good-quality single crystals were obtained after several attempts at recrystallization from water. Crystal 0·65 × 0·06 × 0·04 mm. CAD-4 diffractometer, Mo $K\alpha$ radiation, graphite monochromator. Lattice parameters from the setting angles of 25 reflections ($16 < \theta < 18°$) automatically centred on the diffractometer. Standard procedures (Jones, Hursthouse, Malik & Wilkinson, 1979) followed for collection and reduction of data. ω–2θ-scan mode, ω-scan width $(0{\cdot}85 + 0{\cdot}35\tan\theta)°$, ω-scan speed 1·33–6·67° min^{-1}; $1{\cdot}5 < \theta < 27°$; $h = -21 \to 21$, $k = -15 \to 15$, $l = 0 \to 8$. 5647 reflections measured, 5494 unique, 4724 observed $[F_o > 3\sigma(F_o)]$, merging $R = 0{\cdot}012$. Two standards monitored every 1 h of exposure time indicated only minor fluctuations in intensities. Empirical absorption correction (transmission factors 0·927–0·999) applied to the data. Structure solved by direct methods (Sheldrick, 1984) and refined (on F) by full-matrix least squares (Sheldrick, 1980) using 4724 observed F_o values. All H atoms located from difference maps, isotropic; other atoms anisotropic. In the final cycles of refinement, an isotropic extinction correction parameter e was also varied in the modified expression for the calculated structure factor, $F_c' = F_c(1 - 0{\cdot}0001eF_c^2/\sin\theta)$, which refined to 0·0110 (6). Final R, wR and S respectively 0·054, 0·075 and 3·89 for 4724 observed and 0·063, 0·075 and 2·05 for all 5494 reflections. Total number of parameters refined 418. Max. $\Delta/\sigma = 0{\cdot}15$ [y for H(1A)]. $w = 3{\cdot}1032/[\sigma^2(F_o) + 0{\cdot}0008F_o^2]$ with $\sigma(F_o)$ obtained from counting statistics. Residual electron density in final difference map (absolute value $< 0{\cdot}92$ e Å^{-3}) was of no stereochemical significance. Scattering factors from Stewart, Davidson & Simpson (1965) for H, from Cromer &

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* Saccharin is 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide.

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Table 1. *Fractional coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å$^2 \times 10^3$) *with e.s.d.'s in parentheses*

	x	y	z	U_{eq}*
K(1)	6290 (1)	−1422 (1)	2693 (1)	31·2
K(2)	4384 (1)	3757 (1)	3280 (1)	31·8
Na(1)	3799 (1)	9232 (1)	523 (2)	31·9
S(1)	6171 (1)	1434 (1)	4672 (1)	22·3
O(11)	5556 (2)	4078 (2)	5706 (4)	46
O(12)	6165 (2)	789 (2)	2793 (3)	32
O(13)	6056 (2)	707 (2)	6253 (3)	38
N(11)	5499 (2)	2165 (2)	5124 (4)	28
C(11)	5928 (2)	3332 (3)	5318 (4)	26
C(12)	6911 (2)	3633 (2)	4989 (4)	23
C(13)	7550 (2)	4735 (3)	5005 (5)	33
C(14)	8425 (2)	4779 (4)	4635 (5)	38
C(15)	8656 (2)	3767 (4)	4250 (5)	42
C(16)	8014 (2)	2655 (3)	4194 (5)	39
C(17)	7153 (2)	2637 (3)	4588 (4)	23
S(2)	6691 (1)	5909 (1)	908 (1)	24·6
O(21)	6302 (2)	2766 (2)	−31 (3)	33
O(22)	6612 (2)	6423 (2)	2908 (3)	35
O(23)	6553 (2)	6592 (2)	−460 (4)	46
N(21)	6090 (2)	4553 (2)	766 (4)	27
C(21)	6594 (2)	3850 (2)	209 (4)	22
C(22)	7566 (2)	4505 (2)	−134 (4)	22
C(23)	8257 (2)	4066 (3)	−696 (4)	32
C(24)	9106 (2)	4870 (4)	−962 (5)	41
C(25)	9258 (2)	6071 (4)	−662 (5)	39
C(26)	8560 (2)	6514 (3)	−86 (5)	30
C(27)	7723 (2)	5703 (2)	159 (4)	22
S(3)	1662 (1)	−263 (1)	515 (1)	27·3
O(31)	3225 (1)	1448 (2)	3674 (3)	32
O(32)	1809 (2)	147 (3)	−1425 (3)	47
O(33)	1203 (2)	−1497 (2)	676 (4)	44
N(31)	2578 (2)	147 (2)	1303 (4)	29
C(31)	2580 (2)	949 (2)	2853 (4)	23
C(32)	1730 (2)	1197 (2)	3488 (4)	22
C(33)	1491 (2)	1924 (3)	5072 (5)	30
C(34)	648 (2)	1991 (3)	5402 (6)	37
C(35)	64 (2)	1380 (3)	4159 (5)	37
C(36)	292 (2)	652 (3)	2579 (5)	32
C(37)	1134 (2)	582 (3)	2290 (4)	25
O(1)	4602 (2)	1310 (2)	453 (4)	34

* $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

Table 2. *Distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Interatomic distances involving the K$^+$ and Na$^+$ ions

K(1)–O(12)	2·749 (3)	K(1)–O(22$^{\rm i}$)	2·865 (3)
K(1)–O(23$^{\rm i}$)	3·113 (4)	K(1)–N(11$^{\rm ii}$)	2·889 (4)
K(1)–O(1$^{\rm iii}$)	2·928 (4)	K(1)–O(31$^{\rm ii}$)	2·817 (3)
K(1)–O(32$^{\rm iii}$)	2·959 (3)	K(1)–N(31$^{\rm iii}$)	3·236 (4)
K(2)–O(11)	2·728 (4)	K(2)–N(21)	2·878 (4)
K(2)–O(31)	2·802 (3)	K(2)–O(22$^{\rm iv}$)	2·786 (3)
K(2)–O(23$^{\rm v}$)	2·654 (4)	K(2)–O(11$^{\rm iv}$)	2·599 (4)
Na(1)–O(13$^{\rm iv}$)	2·295 (4)	Na(1)–O(12$^{\rm v}$)	2·290 (4)
Na(1)–O(21$^{\rm v}$)	2·353 (4)	Na(1)–O(1$^{\rm v}$)	2·841 (4)
Na(1)–O(1$^{\rm vi}$)	2·412 (4)	Na(1)–N(31$^{\rm vi}$)	2·538 (4)

Symmetry operations relating the designated atoms to reference atoms at (x, y, z): (i) x, $-1+y$, z; (ii) $1-x$, $-y$, $1-z$; (iii) $1-x$, $-y$, $-z$; (iv) $1-x$, $1-y$, $1-z$; (v) $1-x$, $1-y$, $-z$; (vi) x, $1+y$, z.

Bond lengths and angles in the $C_7H_4NO_3S^-$ anions

	Anion (1) (n = 1)	Anion (2) (n = 2)	Anion (3) (n = 3)
O(n2)–S(n)	1·432 (3)	1·444 (3)	1·441 (4)
O(n3)–S(n)	1·440 (3)	1·440 (3)	1·433 (4)
N(n1)–S(n)	1·596 (5)	1·604 (5)	1·608 (4)
C(n7)–S(n)	1·760 (5)	1·753 (5)	1·770 (5)
C(n1)–O(n1)	1·227 (5)	1·237 (4)	1·244 (4)
C(n1)–N(n1)	1·351 (5)	1·348 (5)	1·353 (4)
C(n2)–C(n1)	1·501 (6)	1·499 (5)	1·490 (5)
C(n3)–C(n2)	1·386 (5)	1·375 (5)	1·390 (5)
C(n7)–C(n2)	1·373 (5)	1·380 (5)	1·378 (5)
C(n4)–C(n3)	1·387 (6)	1·389 (6)	1·383 (6)
C(n5)–C(n4)	1·382 (7)	1·385 (7)	1·386 (6)
C(n6)–C(n5)	1·399 (6)	1·389 (6)	1·383 (6)
C(n7)–C(n6)	1·373 (5)	1·379 (5)	1·385 (5)
O(n3)–S(n)–O(n2)	112·4 (2)	112·8 (2)	114·9 (3)
N(n1)–S(n)–O(n2)	112·7 (2)	112·4 (2)	109·9 (2)
N(n1)–S(n)–O(n3)	112·4 (2)	112·3 (2)	112·1 (3)
C(n7)–S(n)–O(n2)	109·9 (2)	109·8 (2)	110·2 (3)
C(n7)–S(n)–O(n3)	110·8 (2)	110·9 (2)	111·1 (2)
C(n7)–S(n)–N(n1)	97·7 (2)	97·8 (2)	97·2 (2)
C(n1)–N(n1)–S(n)	111·2 (3)	110·8 (3)	111·3 (3)
N(n1)–C(n1)–O(n1)	123·8 (4)	124·6 (4)	124·1 (4)
C(n2)–C(n1)–O(n1)	123·0 (4)	121·6 (4)	122·5 (3)
C(n2)–C(n1)–N(n1)	113·2 (3)	113·8 (3)	113·5 (3)
C(n3)–C(n2)–C(n1)	128·6 (4)	128·9 (4)	128·6 (4)
C(n7)–C(n2)–C(n1)	111·2 (3)	110·7 (3)	111·6 (3)
C(n7)–C(n2)–C(n3)	120·2 (4)	120·4 (4)	119·9 (4)
C(n4)–C(n3)–C(n2)	117·5 (4)	117·6 (4)	118·1 (4)
C(n5)–C(n4)–C(n3)	121·6 (4)	121·6 (4)	121·1 (4)
C(n6)–C(n5)–C(n4)	121·0 (4)	120·8 (4)	121·5 (4)
C(n7)–C(n6)–C(n5)	116·2 (4)	116·7 (4)	116·6 (4)
C(n2)–C(n7)–S(n)	106·7 (3)	106·9 (3)	106·5 (3)
C(n6)–C(n7)–S(n)	129·8 (3)	130·2 (2)	130·6 (2)
C(n6)–C(n7)–C(n2)	123·5 (4)	122·9 (4)	122·9 (4)

Mann (1968) for C, N, O and S, and from Cromer & Waber (1974) for Na$^+$ and K$^+$; f' and f'' values for K and Na from Cromer & Liberman (1970). Calculations performed on a VAX 11/750 computer using the programs *SHELX*80 (Sheldrick, 1980), *SHELXS*84 (Sheldrick, 1984), *XANADU* (Roberts & Sheldrick, 1975) and *SNOOPI* (Davies, 1983).

Discussion. The final atomic parameters, and interatomic distances and angles are given in Tables 1 and 2.*

The structure consists of K$^+$ and Na$^+$ cations, $C_7H_4NO_3S^-$ anions and H_2O molecules in the ratio 2:1:3:1. The contents of the unit cell are shown in Fig. 1. The coordination polyhedra around K(1), K(2) and Na(1), shown in Fig. 2, are highly irregular; K(1) has CN 8, while K(2) and Na(1) each have CN 6. The cations are involved in ionic bonding with the anions through all four potential donor atoms, *i.e.* the amino N, the carbonyl O and the two sulphonyl O atoms, of each anion. The cation–anion bonding is expected to be weak due to some delocalization of the single negative charge on N on to the carbonyl and sulphonyl O atoms. It may be noted, however, that the Na–O distances [2·290 (4)–2·841 (4) Å, mean 2·438 (2) Å] in the present compound are shorter than those [2·304 (2)–2·796 (2) Å, mean 2·478 (1) Å] in the purely Na compound, $Na_3(C_7H_4NO_3S)_3.2H_2O$ (Jovanovski & Kamenar, 1982). The difference in the Na–N distances in the two compounds is even more pronounced [2·538 (4) *vs* 2·731 (3) Å] which suggests stronger Na–saccharinate interaction in the present compound.

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* Anisotropic temperature factors for the non-H atoms, coordinates, bond lengths and angles involving the H atoms, bond angles around the K$^+$ and Na$^+$ ions, selected least-squares-planes and dihedral-angle calculations, and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39580 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The K—O and K—N distances vary from 2·599 (4)–3·113 (4) Å [mean 2·818 (2) Å] and 2·878 (4)–3·236 (4) Å [mean 3·001 (2) Å] respectively. The observed differences between mean K—N and mean K—O and between Na—N and mean Na—O distances (0·183 Å and 0·099 Å respectively) are somewhat larger than that (0·05 Å) expected on the basis of the atomic radii of N and O. However, the differences between mean K—O and mean Na—O and between mean K—N and Na—N distances (0·380 and 0·464 Å respectively) are in accord with the difference (~0·40 Å) in the ionic radii of K^+ and Na^+.

The H_2O molecule is coordinated to one K^+ and two Na^+ ions to produce a polymeric structure. In addition, it participates in moderately strong H bonding with the carbonyl O atoms on two $C_7H_4NO_3S^-$ groups. The dimensions of these H bonds O(1)—H(1*A*)···O(31) and O(1)—H(1*B*)···O(21) are: O(1)—H(1*A*) = 0·76 (5), H(1*A*)···O(31) = 2·18 (5), O(1)···O(31) = 2·847 (6) Å, and ∠O(1)—H(1*A*)—O(31) = 149 (4)°; and O(1)—H(1*B*) = 0·78 (5), H(1*B*)···O(21) = 1·94 (5), O(1)···O(21) = 2·718 (5) Å and ∠O(1)—H(1*B*)—O(21) = 172 (4)°. The dimensions of the three independent $C_7H_4NO_3S^-$ groups are virtually the same and comparable with the corresponding values in other compounds (Haider, Malik, Das & Hursthouse, 1984). They are also planar as indicated by the maximum deviation [0·035 (4) Å] of any atom from the mean plane of the ring atoms. The deviations of the carbonyl O atoms, O(11), O(21) and O(31), from the respective ring planes are 0·015 (3), 0·051 (3) and 0·077 (3) Å respectively. It should be noted that atoms with larger deviations [O(21) and O(31)] are also involved in H bonding.

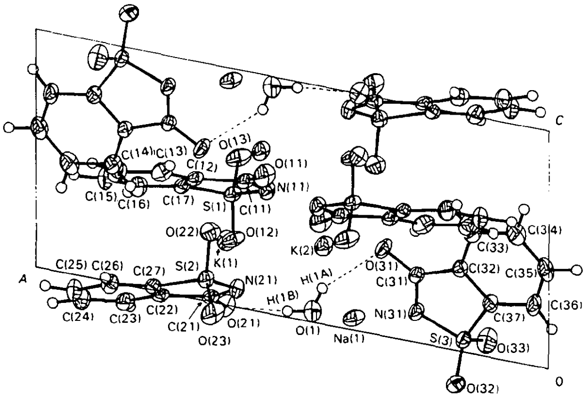

Fig. 1. The crystal structure viewed along **b**. The H atoms are represented by open circles of arbitrary radius, other atoms by thermal ellipsoids with 50% probability. The atom numbering is shown for one asymmetric unit only; the H atoms on the $C_7H_4NO_3S^-$ anions have the same number as the parent C atoms. Atoms plotted constitute two complete asymmetric units related by a centre of symmetry at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. The dashed lines indicate H bonds.

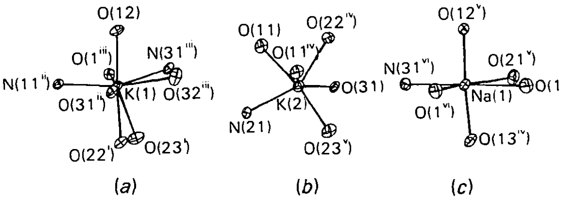

Fig. 2. The environments around (*a*) K(1), (*b*) K(2), and (*c*) Na(1). The designations of the symmetry-generated atoms are the same as in Table 2.

In the crystal, two of the three anions pack nearly parallel to each other (dihedral angle ~4°), whilst the third is inclined to them at ~48°. The shortest interanionic distances are 3·214 (4) and 2·30 (5) Å, between the non-H and H-atom pairs [O(12)···O(21)] and [H(24)···H(24) at (2−*x*, 1−*y*, *z*)] respectively; this suggests only van der Waals interactions between the anions.

KMAM thanks the Association of Commonwealth Universities for the award of a Staff Fellowship and Dhaka University for study leave. We also thank the Bose Centre for Advanced Study and Research, Dhaka University, for financial support of our work on metal–saccharin complexes, and the SERC for support of the crystallographic studies.

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