

Fig. 1. Structure of the title compound. Phenyl H atoms omitted for clarity. Diagram produced by PLUTO (Motherwell, 1976).

1985), which were found to be intermediate between eclipsed and staggered.

The Co—Co bond lengths [average = 2.488 (2) Å] fall well within the range found for the aforementioned comparable compounds (2.462–2.510 Å). The spread of μ_3 C—Co bond lengths at 1.901 (8) to 1.914 (8) Å is less than previously found, e.g. 1.86 (2) to 1.93 (2) Å in $\text{Co}_3(\mu_3\text{-CCH}_3)(\text{CO})_9$

(Sutton & Dahl, 1967). The ethylidyne group is slightly tilted away from the phosphite-coordinated Co atoms; the Co—C(8)—C(9) bond angles are 129.6 (6), 131.6 (6) and 132.2 (6)°, respectively so that the C(8)—C(9) bond is not perfectly normal to the cobalt plane. This effect is also visible in $\text{Co}_3(\mu_3\text{-CCH}_3)(\text{CO})_7\text{dppm}$ and $\text{Co}_3(\mu_3\text{-CCH}_3)(\text{CO})_8(\text{PPh}_3)$, and is presumably due to the steric effect of the bulky ligands.

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Structure of Sodium Thiosaccharinate Monohydrate*

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Abstract. $\text{Na}[\text{C}_7\text{H}_4\text{NO}_2\text{S}_2]\cdot\text{H}_2\text{O}$, $M_r = 239.25$, orthorhombic, $P2_12_12_1$, $a = 7.499$ (3), $b = 26.895$ (10), $c = 4.705$ (2) Å, $V = 948.93$ Å³, $Z = 4$, D_m (pycnometrically) = 1.64, $D_x = 1.675$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.51$ mm⁻¹, $F(000) = 484$, room tem-

perature, final $R = 0.043$ for 792 independent observed reflections. The crystal structure consists of Na^+ cations, thiosaccharinate anions and water molecules. Each Na^+ ion is surrounded by a distorted octahedron composed of two water molecules, three O atoms belonging to the SO_2 groups and one N atom from a thiosaccharinate ion. The Na—O dis-

* Thiosaccharin is 1,2-benzisothiazol-9(2H)-thione 1,1-dioxide.

tances range from 2.366 (6) to 2.451 (6) Å and the angles in the octahedron from 77.1 (2) to 106.6 (2)°. The Na—N distance is 2.512 (6) Å.

Introduction. This study is a continuation of our structural investigations of the metal complexes of saccharin and thiosaccharin. Several crystal structures of saccharinate complexes with metals are known, while there are no structural examples of metal complexes with thiosaccharin. Therefore, we have undertaken a systematic study of different metal complexes with thiosaccharin. Here we report the crystal structure determination of sodium thiosaccharinate monohydrate and compare its structural characteristics with those found for the analogous sodium saccharinate hydrate and other metal saccharinates.

Experimental. The compound was synthesized for the first time by addition of an alcoholic solution of thiosaccharin to an aqueous solution of sodium chloride. The mixture was refluxed up to 373 K for 15 min. After cooling to room temperature, transparent yellow needle-shaped crystals were obtained. The single crystals were grown by recrystallization from ethanol. Diffraction intensities collected on a Philips PW1100 automatic four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Crystal of dimensions 0.60 × 0.15 × 0.10 mm used for measurement of accurate unit-cell parameters (from 18 reflections with θ between 5 and 11°) and diffraction-data collection. Intensities of reflections with indices h 0 to 10, k 0 to 37, l 0 to 6; ω - 2θ scan technique; scan width 0.9°; scan speed 0.03° s⁻¹; $3 < \theta < 30^\circ$; 885 unique reflections measured; 792 with $I > 3\sigma(I)$ considered observed and used in structure solution and refinement. Intensities of three standard reflections measured every 2 h showed no evidence of crystal decay. Data corrected for Lorentz and polarization effects but not for absorption. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99–101, 149–150). The structure was solved by direct methods (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined (on F) by full-matrix least squares. All H-atom positions from the water molecules and the thiosaccharinate ion located from difference Fourier synthesis. The final least-squares refinement (including 141 variable parameters) assuming anisotropic thermal parameters for non-H atoms and isotropic temperature factors for all H atoms gave the following discrepancy factors: $R = 0.043$, $wR = 0.043$, $w = 0.7631/[\sigma^2(F) + 0.000729(F)^2]$; $(\Delta/\sigma)_{\max} = 0.747$. Max. and min. heights in final difference Fourier map 0.36 and -0.40 e Å⁻³, respectively. All calculations were performed on a UNIVAC1110 computer of the Zagreb University Computing Centre, SRCE,

Table 1. Fractional atomic coordinates ($\times 10^4$ for non-H atoms and $\times 10^3$ for H atoms) and equivalent isotropic thermal parameters U_{eq} (Å² $\times 10^4$ for non-H and Å² $\times 10^2$ for H atoms), with e.s.d.'s in parentheses

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
Na	6861 (3)	2462 (1)	33 (5)	288 (5)
S(1)	4160 (2)	1818 (1)	4986 (4)	219 (3)
S(2)	8726 (3)	1116 (1)	2575 (5)	452 (5)
O(1)	4331 (6)	2209 (2)	7119 (11)	282 (11)
O(2)	2669 (6)	1888 (2)	3102 (10)	308 (11)
C(1)	4108 (10)	1226 (2)	6557 (14)	210 (14)
C(2)	2881 (11)	1011 (3)	8322 (18)	318 (18)
C(3)	3242 (12)	533 (3)	9284 (17)	388 (21)
C(4)	4773 (12)	287 (3)	8485 (18)	365 (20)
C(5)	5986 (11)	507 (3)	6704 (19)	344 (18)
C(6)	5675 (10)	983 (2)	5748 (15)	261 (15)
C(7)	6749 (10)	1309 (3)	3805 (16)	284 (16)
N	6054 (8)	1756 (2)	3284 (12)	265 (12)
O(3 _w)	4460 (7)	2978 (2)	1815 (10)	344 (12)
H(C2)	192 (12)	116 (3)	876 (19)	50 (15)
H(C3)	241 (12)	36 (3)	1053 (18)	50 (15)
H(C4)	508 (12)	-7 (3)	905 (18)	50 (15)
H(C5)	694 (12)	35 (3)	616 (19)	50 (15)
H1(O3 _w)	413	324	62	87 (26)
H2(O3 _w)	484	314	360	87 (26)

with programs written by Domenicano, Spagna & Vacigo (1969) and Sheldrick (1976).

Discussion. The final atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.* Interatomic distances and angles are given in Table 2. A view of the structure with the atom-labelling scheme is given in Fig. 1 and Fig. 2 shows the crystal packing.

The structure consists of Na⁺ cations, thiosaccharinate anions and water molecules. Each Na⁺ ion is irregularly six coordinated, being surrounded by two O atoms from the water molecules, three O atoms belonging to the SO₂ groups and one N atom from the five-membered ring of the thiosaccharinate ion (Fig. 1). The Na—O distances for water molecules range from 2.423 (6) to 2.440 (6) Å [mean 2.315 (6) Å] and those for SO₂ from 2.366 (6) to 2.451 (6) Å [mean 2.424 (6) Å, Table 2]. These mean values for Na—O distances are shorter than those found in dipotassium sodium trisaccharinate monohydrate, K₂Na(C₇H₄NO₃S)₃·H₂O (I) [2.290 (4)–2.841 (4) Å, mean 2.438 (2) Å] (Malik, Haider, Hossain, & Hursthouse, 1984) and in the purely trisodium trisaccharinate dihydrate, Na₃(C₇H₄NO₃S)₃·2H₂O (II) [2.304 (2)–2.796 (2) Å, mean 2.478 (2) Å] (Jovanovski & Kamenar, 1982). The

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53127 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å), angles (°) and the geometry around the Na⁺ ions

S(1)—N	1.639 (6)	C(1)—C(6)	1.397 (10)
S(1)—O(1)	1.458 (5)	C(1)—C(2)	1.367 (11)
S(1)—O(2)	1.439 (5)	C(2)—C(3)	1.391 (11)
S(1)—C(1)	1.757 (6)	C(3)—C(4)	1.376 (12)
N—C(7)	1.332 (9)	C(4)—C(5)	1.371 (12)
C(7)—S(2)	1.675 (8)	C(5)—C(6)	1.378 (10)
C(6)—C(7)	1.501 (10)		
S(1)—N—C(7)	109.9 (7)	C(1)—C(6)—C(5)	119.2 (7)
C(1)—S(1)—N	97.6 (3)	C(5)—C(6)—C(7)	130.6 (7)
O(1)—S(1)—O(2)	113.5 (3)	S(1)—C(1)—C(6)	106.9 (5)
O(1)—S(1)—C(1)	111.5 (3)	S(1)—C(1)—C(2)	130.8 (6)
O(1)—S(1)—N	109.5 (3)	C(2)—C(1)—C(6)	122.3 (6)
O(2)—S(1)—N	112.7 (3)	C(1)—C(2)—C(3)	117.2 (7)
O(2)—S(1)—C(1)	111.1 (3)	C(2)—C(3)—C(4)	121.2 (8)
N—C(7)—C(6)	115.4 (6)	C(3)—C(4)—C(5)	120.9 (7)
N—C(7)—S(2)	124.2 (6)	C(4)—C(5)—C(6)	119.2 (7)
S(2)—C(7)—C(6)	120.3 (5)	C(1)—C(6)—C(7)	110.1 (6)
Na...O(3w)	2.423 (6)	Na...O(1) ⁱⁱⁱ	2.451 (6)
Na...O(3w) ⁱ	2.440 (6)	Na...O(2) ^j	2.366 (6)
Na...O(1) ⁱⁱ	2.438 (6)	Na...N	2.512 (6)

Symmetry code: (i) 0.5 + x, 0.5 - y, -z; (ii) x, y, -1 + z; (iii) 0.5 + x, 0.5 - y, 1 - z; (iv) -0.5 + x, 0.5 - y, -z; (v) 0.5 - x, 0.5 - y, -z.

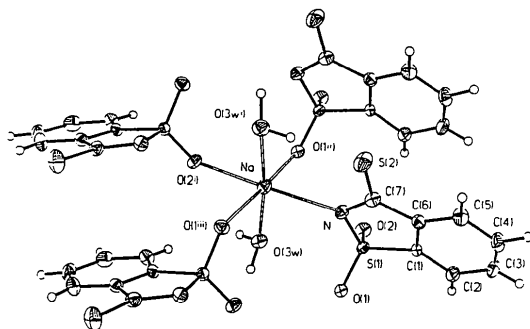


Fig. 1. A view of the structure with the atom-labelling scheme.

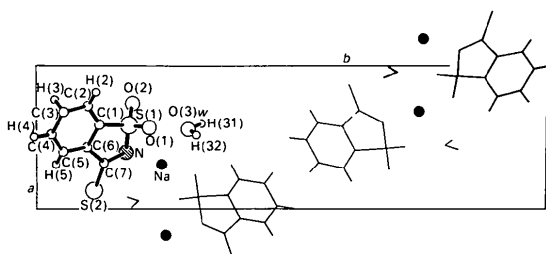


Fig. 2. The crystal packing.

difference in the Na—N distances in the three compounds mentioned above is even more significant [2.512 (6) Å in the present compound, 2.538 (4) Å in (I) and 2.731 (3) Å in (II)]. This suggests a stronger interaction between the thiosaccharinate and Na⁺ than that between the saccharinate and Na⁺. Also, rather than the highly irregular polyhedra around the Na⁺ ions in the structures of (I) and (II) the

Table 3. Interatomic distances (Å) and angles (°) within the thiazole ring of the thiosaccharinate ion in the present compound and in the analogous structures of the Na and mixed K₂Na saccharinate

The atom-labelling scheme used is that from the present paper.

	Na saccharinate	K ₂ Na saccharinate	Na thiosaccharinate
C(1)—C(6)	1.382 (4)	1.373 (5)	1.397 (10)
	1.384 (4)	1.380 (5)	
	1.389 (3)	1.378 (5)	
C(6)—C(7)	1.506 (3)	1.501 (6)	1.501 (10)
	1.496 (3)	1.499 (5)	
	1.494 (3)	1.490 (5)	
C(7)—N	1.354 (3)	1.351 (5)	1.332 (9)
	1.346 (3)	1.348 (5)	
	1.357 (4)	1.353 (4)	
N—S(1)	1.596 (2)	1.596 (5)	1.639 (6)
	1.606 (2)	1.604 (5)	
	1.603 (2)	1.608 (4)	
S(1)—C(1)	1.764 (2)	1.760 (5)	1.757 (6)
	1.767 (2)	1.753 (5)	
	1.764 (3)	1.770 (5)	
C(6)—C(7)—N	113.0 (2)	111.2 (3)	115.4 (6)
	113.7 (2)	113.8 (3)	
	113.5 (2)	113.5 (3)	
C(7)—N—S(1)	111.4 (2)	111.2 (3)	109.9 (7)
	111.3 (2)	110.8 (3)	
	111.0 (2)	111.3 (3)	
N—S(1)—C(1)	97.9 (1)	97.7 (2)	97.6 (3)
	97.5 (1)	97.8 (2)	
	97.8 (1)	97.2 (2)	
S(1)—C(1)—C(6)	106.2 (2)	106.7 (3)	106.9 (5)
	106.4 (2)	106.9 (3)	
	106.3 (2)	106.5 (3)	
C(1)—C(6)—C(7)	111.2 (2)	111.2 (3)	110.1 (6)
	111.1 (2)	110.7 (3)	
	111.3 (2)	111.6 (3)	

polyhedron around the Na⁺ ion in the present structure is less distorted and can be described as a distorted octahedron with angles ranging from 77.1 (2) to 106.6 (2)°.

The O(3w)···S(2^{iv}) distance of 3.242 (7) Å indicates the existence of hydrogen bonding between thiosaccharinate ion and water molecule.

As indicated by the maximum deviation (0.015 Å) of any atom from the mean plane of the six- and five-membered rings, the thiosaccharinate ion is essentially planar. The angle between the planes through the five- and six-membered rings is 0.5°.

Interatomic distances and angles within the thiosaccharinate ion in the present compound are in general close to the corresponding values found in the analogous saccharinate ion in the structures of Na and Mg saccharinates (Jovanovski & Kamenar, 1982), in (I), in Mn^{II} saccharinate (Kamenar & Jovanovski, 1982) and the corresponding isomorphous Fe^{II}, Co^{II}, Ni^{II}, Zn^{II}, Cu^{II}, Cd^{II} and Cr^{II} saccharinates (Haider, Malik, Ahmed, Hess, Riffel & Hursthouse, 1983; Haider, Malik, Das & Hursthouse, 1984; Cotton, Lewis, Murillo, Schwotzer & Valle, 1984), and in Sn^{IV} saccharinate (Chuprunov, Gromilov, Stolyarova, Tarkhova & Belov, 1982) as

well as in Pb^{II} saccharinate (Jovanovski, Hergold-Brundić & Kamenar, 1988), Hg^{II} saccharinate (Kamenar, Jovanovski & Grdenić, 1982) and chloromercury (II) saccharinate (Jovanovski, Kamenar, Ferguson & Kaitner, 1988). Since a complete comparison is difficult, we focused our attention on the interatomic distances and angles within the thiazole ring of the thiosaccharinate ion in the present compound and the corresponding values in the analogous structures of (I) and (II) (see Table 3). In spite of the general similarity, there are small differences in some bond lengths and angles. Namely, in (I) and (II) the C(7)—N bonds are longer than in the Na thiosaccharinate, while the N—S(1) bonds are shorter and the C(6)—C(7)—N angles are smaller. These differences are probably mainly due to the substitution of the O atom from the C=O group in the saccharinate ion by the S atom in the analogous thiosaccharinate ion.

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Structure of Tetrakis(2,3-dihydro-1,3-thiazole-2-thione)palladium(II) Dichloride 2,3-Dihydro-1,3-thiazole-2-thione Solvate

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Abstract. [Pd(C₃H₃NS₂)₄]Cl₂·C₃H₃NS₂, *M*_r = 763·2, monoclinic, *P*2₁/*c*, *a* = 11·546 (1), *b* = 17·749 (2), *c* = 13·724 (2) Å, β = 100·91 (1)°, *V* = 2761·6 Å³, *Z* = 4, *D*_x = 1·835, *D*_m = 1·83 (1) Mg m⁻³, *F*(000) = 1520, *T* = 295 K, Mo *K*α, λ = 0·71073 Å, μ = 1·60 mm⁻¹, *R* = 0·0252 for 4086 observed reflections. Thiazoline-2-thione, *tztH*, is monodentate S-donating to Pd^{II} in the [Pd(*tztH*)₄]²⁺ cation with a mean Pd—S distance of 2·336 (1) Å and a mean S—Pd—S angle of 90·2 (1)°. The chloride ions form an extensive H-bonding network involving the imido (NH) groups of the ligands and the solvated *tztH* molecule with NH...Cl distances ranging from 3·051 to 3·561 Å.

Introduction. Thioamides coordinate readily with divalent palladium and platinum generally producing complexes of formula [ML₂Cl₂] and [ML₄]Cl₂, although compounds with other stoichiometries have also been reported (Raper, 1985). Structural details are limited to the *cis* isomer of [Pd(thiazolidine-2-thione)₂Cl₂], for the [ML₂Cl₂] compounds (Kubiak, 1985). The situation is slightly better for the [PdL₄]Cl₂ series where structures have been reported for thiorea (tu) (Berta, Spofford, Boldrini & Amma, 1970), 1-methylimidazoline-2-thione (mimntH) (Butler, Creighton, Oughtred, Raper & Nowell, 1983) and thiazolidine-2-thione (*tztH*) (Kubiak &