

9-ethylguanine, 1,3-dimethylxanthine and 1,3,9-trimethylxanthine), the Pt—N bond distances involving the tmen ligand lie in the range 2.00 (4) to 2.075 (6) Å (Orbell, Taylor, Birch, Lawton, Vilkins & Keefe, 1988). In the perchlorate salt of the [PtCl(H₂C=CH₂)(tmen)] cation, the Pt—N bond distance *trans* to the Cl atom is 2.084 (2) Å and the other Pt—N distance is 2.119 (2) Å (Gervasio, Mason, Maresca & Natile, 1986). Similarly in the structure of [PtCl(1-methylcytosine)(tmen)]ClO₄ (Preut, Frommer & Lippert, 1990), the Pt—N bond *trans* to the Cl atom is 2.078 (4) Å and the other Pt—N distance, *trans* to the nucleobase, is 2.066 (4) Å. The Pt—N bond distance of 2.141 (5) Å found in [Pt(C₆F₅)₂(tmen)] is significantly longer than in any of complexes cited above and reflects the greater *trans* influence of the pentafluorophenyl groups (Appleton, Clark & Manzer, 1973).

There are two other compounds containing the *cis*-Pt(C₆F₅)₂ entity that have been structurally characterized. In the structure of [Pt(C₆F₅)₂(C₆H₅C≡CC₆H₅)₂], a molecule with a two-fold symmetry axis, the Pt—C bond distance involving the pentafluorophenyl group is 2.048 (3) Å (Usón, Forniés, Tomás, Menjón & Welch, 1986). In the structure of [Pt(C₆F₅)₂{SC(S)P(C₆H₁₁)₃}(CO)], the Pt—C bond distance *trans* to the S atom is 2.056 (6) Å and the other Pt—C distance is 2.045 (7) Å (Usón, Forniés, Usón, Yagüe, Jones & Meyer-Bäse, 1986). The relatively long Pt—C bond distances in these structures may be contrasted to the Pt—C bond distance of 2.006 (6) Å found in [Pt(C₆F₅)₂(tmen)]. This study demonstrates that the

tmen ligand has a weaker *trans* influence than an acetylene molecule.

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Structure of Potassium Thiosaccharinate Monohydrate*

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Abstract. K[C₇H₄NO₂S₂].H₂O, *M_r* = 255.36, orthorhombic, *Pbca*, *a* = 8.873 (1), *b* = 27.108 (6), *c* = 8.708 (1) Å, *V* = 2094.5 Å³, *Z* = 8, *D_x* =

1.62 Mg m⁻³, λ(Mo Kα) = 0.71069 Å, μ = 0.81 mm⁻¹, *F*(000) = 1032, room temperature, final *R* = 0.032 for 1801 observed unique reflections. The structure is built up of K⁺ cations, thiosaccharinate anions and water molecules. The K⁺ ion is six

* Thiosaccharin is 1,2-benzisothiazol-3(2*H*)-thione 1,1-dioxide.

coordinated to two water O atoms, three O atoms from the SO₂ groups and one N atom from the thiosaccharinate ion. The K—O distances range from 2.722 (3) to 3.158 (3) Å, while the K—N distance is 2.825 (2) Å. The coordination polyhedron is irregular.

Introduction. Recently we reported the results of the crystal structure investigation of sodium thiosaccharinate monohydrate (Penavić, Jovanovski & Grupče, 1990). In order to extend this investigation we have prepared a series of different metal complexes with thiosaccharin, and we report here the crystal structure of potassium thiosaccharinate monohydrate.

Experimental. The title compound was prepared for the first time by addition of an equimolar ethanolic solution of thiosaccharin to an aqueous solution of potassium hydroxide. The transparent yellow prismatic crystals were obtained after cooling to room temperature the reaction mixture previously heated under reflux up to 373 K for 15 min. The single crystals, suitable for X-ray crystallography, were grown at room temperature from ethanol. Intensity data collected on a Philips PW1100 automatic four-circle diffractometer, graphite-monochromated Mo K α radiation. Crystal dimensions 0.21 × 0.28 × 0.33 mm. Accurate unit-cell parameters determined by a least-squares fit for 18 reflections having $5 < \theta < 11^\circ$. Intensities of reflections with indices $h0$ to 12, $k0$ to 38, $l0$ to 12; ω - 2θ scan technique; scan width 1.20°; scan speed 0.04 s⁻¹; $2 < \theta < 30^\circ$; 2186 unique reflections measured, 1801 with $I > 5\sigma(I)$ used in structure solution and refinement. Three standard reflections measured every 2 h of exposure time showed no significant variations during data collection. Intensity data corrected for Lorentz-polarization factors 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. E map gave positions of all non-H atoms. H atoms located from difference Fourier synthesis. All H(C) atoms included in the refinement with one common isotropic thermal parameter, H(O_w) atom positions not refined. The final cycle of refinement (including 141 variable parameters) assuming anisotropic thermal parameters for non-H atoms converged to $R = 0.032$, $wR = 0.039$, $(\Delta/\sigma)_{\max} = 0.254$, $w = 1/[\sigma^2(F) + 0.004232(F)^2]$. Max. and min. heights in final difference Fourier map 0.27 and $-0.37 e \text{ \AA}^{-3}$, respectively. All calculations performed on a UNIVAC 1110 computer of the Zagreb University Computing Centre, SRCE, with programs written by

Table 1. Fractional atomic coordinates ($\times 10^4$ for non-H and $\times 10^3$ for H atoms) and thermal parameters U_{eq} ($\text{\AA}^2 \times 10^4$ for non-H atoms) and U_{iso} ($\text{\AA}^2 \times 10^2$ 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	$U_{\text{eq}}/U_{\text{iso}}$
K	2672 (1)	286.3 (2)	-2470 (1)	428 (1)
S(1)	-430 (1)	734.6 (2)	865 (1)	308 (1)
S(2)	1658 (1)	1508.4 (3)	-2528 (1)	552 (2)
O(1)	-1761 (2)	450 (1)	513 (2)	439 (4)
O(2)	455 (3)	534 (1)	2105 (2)	537 (5)
N	569 (2)	814 (1)	-671 (2)	367 (4)
C(1)	-860 (2)	1358 (1)	1194 (2)	311 (4)
C(2)	-1742 (3)	1571 (1)	2321 (3)	450 (5)
C(3)	-1896 (4)	2085 (1)	2250 (3)	518 (6)
C(4)	-1142 (4)	2363 (1)	1149 (3)	501 (6)
C(5)	-252 (3)	2136 (1)	46 (3)	408 (5)
C(6)	-128 (2)	1627 (1)	61 (3)	305 (4)
C(7)	690 (2)	1295 (1)	-1017 (3)	337 (4)
O(3 _w)	4869 (3)	602 (1)	-523 (3)	700 (6)
H1(O3 _w)	518	98	-86	164 (18)
H2(O3 _w)	532	59	-49	164 (18)

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

S(1)—N	1.619 (2)	C(1)—C(2)	1.382 (3)
S(1)—O(1)	1.443 (2)	C(2)—C(3)	1.400 (4)
S(1)—O(2)	1.442 (2)	C(3)—C(4)	1.392 (4)
S(1)—C(1)	1.757 (2)	C(4)—C(5)	1.388 (4)
N—C(7)	1.343 (3)	C(5)—C(6)	1.384 (3)
C(7)—S(2)	1.675 (2)	O(3 _w)—H1(O3 _w)	1.099 (3)
C(6)—C(7)	1.488 (3)	O(3 _w)—H2(O3 _w)	0.965 (3)
C(1)—C(6)	1.387 (3)		
S(1)—N—C(7)	110.9 (2)	C(1)—C(6)—C(7)	111.1 (2)
C(1)—S(1)—N	97.3 (1)	C(1)—C(6)—C(5)	119.4 (2)
O(1)—S(1)—O(2)	113.7 (1)	C(5)—C(6)—C(7)	129.4 (2)
O(1)—S(1)—C(1)	111.8 (1)	S(1)—C(1)—C(6)	106.6 (2)
O(1)—S(1)—N	110.1 (1)	S(1)—C(1)—C(2)	129.8 (2)
O(2)—S(1)—N	111.7 (1)	C(2)—C(1)—C(6)	123.5 (2)
O(2)—S(1)—C(1)	111.1 (1)	C(1)—C(2)—C(3)	116.0 (2)
N—C(7)—C(6)	114.0 (2)	C(2)—C(3)—C(4)	121.5 (3)
N—C(7)—S(2)	123.5 (2)	C(3)—C(4)—C(5)	120.6 (3)
S(2)—C(7)—C(6)	122.4 (2)	C(4)—C(5)—C(6)	118.8 (2)
K—O(1 ⁱⁱ)	2.746 (2)	K—O(3 _w)	2.722 (3)
K—O(1 ⁱⁱⁱ)	2.733 (2)	K—O(3 _w ⁱ)	3.159 (3)
K—O(2 ^v)	2.800 (2)	K—N	2.825 (2)

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

Domenicano, Spagna & Vaciago (1969) and Sheldrick (1976).

Discussion. Fractional atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.* Interatomic distances and angles are given

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53958 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

in Table 2. A view of the structure showing the environment around K^+ and the atom-labelling scheme is given in Fig. 1. Fig. 2 shows the arrangement of the structural constituents in the unit cell. The structure consists of K^+ cations, thiosaccharinate anions and the water molecules. Each potassium cation is surrounded by five O atoms, three from the SO_2 groups, two from water molecules and one N atom from the thiosaccharinate anion (Fig. 1). Similarly to the mixed K_2Na saccharinate monohydrate, $K_2Na[C_7H_4NO_3S]_3 \cdot H_2O$, (I), the polyhedron around the K^+ ion in the present structure is highly irregular. The mean $K-O$ distance for SO_2 groups [2.760 (2) Å, Table 2] is shorter than the corresponding one found in (I) [2.599 (4)–3.113 (4) Å, mean 2.787 (4) Å] (Malik, Haider, Hossain & Hursthouse, 1984). The discrepancy between the $K-N$ distances in the two above mentioned compounds is even more pronounced [2.825 (2) Å in the present determination and mean 3.001 (4) Å in (I)]. These shorter $K-O$ and $K-N$ distances indicate stronger interaction between the thiosaccharinate anion and K^+ cation. A similar result was obtained in the case of the

corresponding Na saccharinate (II) and Na thiosaccharinate (III).

The water molecule is coordinated to the K^+ cations, at the same time participating in hydrogen bonding with the S atom from the $C=S$ group and one O atom from the SO_2 group. The geometry of the two hydrogen bonds of the $O_w-H \cdots S$ and $O_w-H \cdots O$ type is: $O(3w)-H1(O3w) = 1.099$ (3), $H1(O3w) \cdots S(2^{iii}) = 2.398$ (1), $O(3w) \cdots S(2^{iii}) = 3.381$ (3) Å, $\angle O(3w)-H1(O3w)-S(2^{iii}) = 148.0$ (2)°; $O(3w)-H2(O3w) = 0.965$ (3), $H2(O3w) \cdots O(2^v) = 2.107$ (2), $O(3w) \cdots O(2^v) = 3.027$ (4) Å, $\angle O(3w)-H2(O3w)-O(2^v) = 158.9$ (2)°; $\angle H1(O3w)-O(3w)-H2(O3w) = 100.3$ (3)°; $\angle S(2)-O(3w)-O(2^v) = 117.2$ (3)°. [The labels (iii) and (v) refer to the equivalent positions given in Table 2.]

The thiosaccharinate ion is planar [max. deviation 0.036 (5) Å for C(3) atom, angle between the best planes through the five- and six-membered rings 2.1°]. Bond lengths and angles within the thiosaccharinate ion are, in general, close to the corresponding values found in the analogous ionic structures (II) (Jovanovski & Kamenar, 1982) and (III) (Penavić, Jovanovski & Grupče, 1990) as well as in other ionic saccharinates (Kamenar & Jovanovski, 1982; Haider, Malik, Ahmed, Hess, Riffel & Hursthouse, 1983; Haider, Malik, Das & Hursthouse, 1984; Jovanovski, Hergold-Brundić & Kamenar, 1988).

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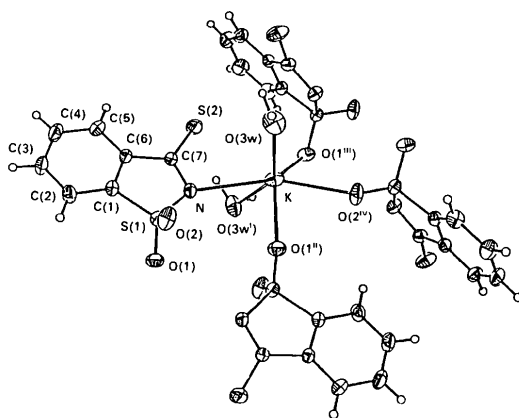


Fig. 1. View of the structure showing the environment around K, the atom labelling and vibrational ellipsoids at the 50% probability level (ORTEP; Johnson, 1976).

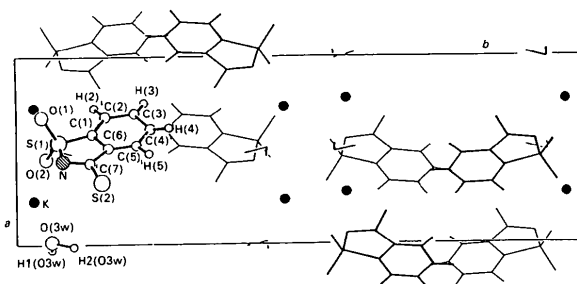


Fig. 2. The packing of the structural constituents in the unit cell.

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