

A New Supramolecular Assembly Obtained by Reaction Between Thiosaccharin and Pyridine

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The crystal structure of pyridinium thiosaccharinate thiosaccharin, $[\text{HNC}_5\text{H}_5]^+ [(\text{tsac})(\text{Htsac})]^-$ ($\text{Htsac} = \text{C}_7\text{H}_5\text{NO}_2\text{S}_2$, the thiosaccharin molecule), was determined by single-crystal X-ray diffraction. Both, the thiosaccharinate anion, the corresponding neutral molecule and the pyridinium cation are nearly planar and arranged in the solid state in an almost parallel fashion, hence giving rise to a layered supramolecular structure. The anion shows small but significant modifications in the bonding of the thioamide group as compared with the neutral molecule. The crystal is further stabilized by an extensive H-bonding network. The FTIR spectrum of the compound is briefly commented.

Key words: Pyridinium Thiosaccharinate Thiosaccharin, Crystal Structure, Supramolecular Adduct, IR Spectra

Introduction

In the last years we have synthesized and characterized a number of metal complexes of thiosaccharin (for a recent review *cf.* [1]), and have recently initiated a search for supramolecular adducts of thiosaccharin with some simple organic amines. Recently, we presented the first results of this investigation, describing the synthesis and characterization of a compound generated by interaction of thiosaccharin with hexamethylenediamine [2]. In this paper a second example of this type, an adduct obtained by the reaction of thiosaccharin with pyridine, is described.

Results and Discussion

Crystal structure

An ORTEP [3] drawing of the structure is presented in Fig. 1. The most remarkable aspect of this new structure is the simultaneous presence of a thiosaccharinate anion and a neutral thiosaccharin molecule in the crystal structure. Selected bond lengths and angles are given in Table 1. As expected, the thiosaccharinate anion (*tsac*) and the neutral thiosaccharin molecule (*Htsac*) are nearly planar (rms distance of

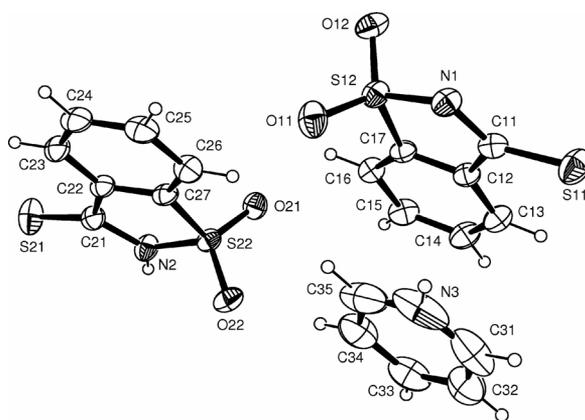


Fig. 1. Molecular structures of the components of $[\text{HNC}_5\text{H}_5]^+ [(\text{tsac})(\text{Htsac})]^-$ in the crystal (ORTEP-II [3], displacement ellipsoids at the 30% probability level) with crystallographic numbering scheme.

atoms from the least-squares planes equal to 0.010 Å for *tsac* and 0.017 Å for *Htsac*). Bond lengths and angles for *tsac* agree well with those reported for the sodium, potassium and ammonium thiosaccharinate salts [4–6]. Molecular dimensions for *Htsac* are also in accord with the corresponding structural data previously reported for the free molecule [7].

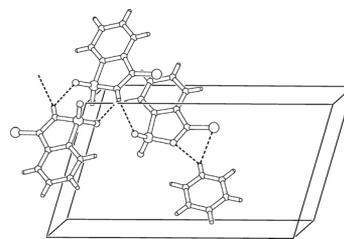
Table 1. Selected bond lengths (Å) and angles (deg) in $[\text{HNC}_5\text{H}_5]^+ [(\text{tsac})(\text{Htsac})]^-$.

C(31)–N(3)	1.296(7)	S(22)–N(2)	1.662(2)
C(35)–N(3)	1.299(7)	C(11)–N(1)	1.322(4)
C(21)–N(2)	1.358(4)	C(11)–S(11)	1.667(3)
C(21)–C(22)	1.478(4)	C(12)–C(17)	1.374(4)
C(21)–S(21)	1.629(3)	C(17)–S(12)	1.772(2)
C(22)–C(27)	1.385(4)	S(12)–O(11)	1.430(2)
S(22)–O(21)	1.424(2)	S(12)–O(12)	1.433(2)
S(22)–O(22)	1.424(2)	S(12)–N(1)	1.632(2)
C(35)–N(3)–C(31)	122.2(4)	N(1)–C(11)–C(12)	113.1(2)
N(2)–C(21)–S(21)	124.8(2)	C(12)–C(11)–S(11)	122.6(2)
C(22)–C(21)–S(21)	126.8(2)	O(11)–S(12)–O(12)	115.8(1)
N(2)–S(22)–C(27)	91.6(1)	O(11)–S(12)–N(1)	111.1(1)
C(21)–N(2)–S(22)	117.0(2)	N(1)–S(12)–C(17)	95.9(1)
O(21)–S(22)–O(22)	116.8(1)	C(11)–N(1)–S(12)	112.4(2)

By comparing with the structure of the neutral thiosaccharin molecule, it can be noted that the major changes in the anionic thiosaccharinate moiety occur at the thioamide group. This anionic function is dominated by delocalized N–C–S bonding. This is shown by the shortening of the N–C bond (from 1.358(4) Å in neutral Htsac to 1.322(4) Å in tsac), and also by the lengthening of the C–S bond (from 1.629(3) Å in Htsac to 1.667(3) Å in tsac). Significant lengthening is also observed in the C1–C2 bond (from 1.478(4) to 1.500(3) Å) and the S2–C7 distance (from 1.755(2) to 1.772(2) Å). In contrast, no significant changes are observed for $Ci2-Ci7$ and sulfonyl $Si1=O$ ($i = 1, 2$) bonds when comparing the neutral ($i = 2$) and charged ($i = 1$) molecules.

The tsac and Htsac moieties and the $[\text{HNC}_5\text{H}_5]^+$ cation are arranged almost parallel in the solid state giving rise to a layered crystal packing. The $[\text{HNC}_5\text{H}_5]^+$ cation is nearly coplanar to a neighboring tsac anion to which it is further linked through bifurcated $\text{pyrH}\cdots\text{N}(\text{tsac})$ and $\text{pyrH}\cdots\text{S}$ bonds ($d(\text{N}3\cdots\text{N}1) = 2.980$ Å and $d(\text{N}3\cdots\text{S}11) = 3.328$ Å). The neutral Htsac molecules are arranged in the crystal as centrosymmetric dimers linked through a pair of N–H \cdots O bonds ($d(\text{N}2\cdots\text{O}22') = 2.909$ Å). Neighboring $\text{Hpyr}\cdots\text{tsac}$ and $\text{Htsac}\cdots\text{Htsac}$ dimers are bound to each other through $\text{Htsac}\cdots\text{O}(\text{tsac})$ interactions ($d(\text{N}2\cdots\text{O}12'') = 3.028$ Å). Fig. 2 shows a view of the crystal packing with the H-bonding network along the crystallographic a axis. Details of H-bonding parameters are provided as supplementary material.

In the case of the recently described adduct of saccharin, $[\text{HNC}_5\text{H}_5]^+ [\text{sac}]^-$, the pyridinium and saccharinate ions are linked by intermolecular N–H \cdots O hydrogen bonds into discrete assemblies. Anions and

Fig. 2. Crystal packing of $[\text{HNC}_5\text{H}_5]^+ [(\text{tsac})(\text{Htsac})]^-$ as viewed along the crystallographic a axis. H bonds are indicated by dashed lines (PLATON [8]).

cations form two symmetry-independent stacks running along the crystallographic a axis, in which anions and cations alternate [9].

Infrared spectra

The spectrum is very complex, especially in the range below 1700 cm^{-1} in which both pyridine [10] and thiosaccharin [7, 11] show a large number of bands.

Interestingly, the spectra allow no definite differentiation of bands related to thiosaccharin and its anion. Probably, this effect is caused in part by the participation of both species in hydrogen bonding in the crystal lattice, which produces band broadening. Notwithstanding, three of the most typical thiosaccharin bands, *i. e.* the two SO_2 stretching modes and the $\nu(\text{CS})$ mode appear displaced to lower energies in the adduct, when compared with their position in free thiosaccharin ($\nu_{\text{as}}(\text{SO}_2)$ from 1376 to 1352 cm^{-1} , $\nu_{\text{s}}(\text{SO}_2)$ from 1156 to 1141 cm^{-1} and $\nu(\text{CS})$ from 1039 to 1018 cm^{-1}). Also the $\nu(\text{NC})$ and $\nu(\text{NS})$ bands of thiosaccharin, although coupled with other vibrations, are displaced to lower wavenumbers in the adduct.

Experimental Section

Synthesis of the adduct

Thiosaccharin (1,2-benzisothiazol-3(2H)-thione-1,1-dioxide) was obtained by heating a mixture of 0.1 mol of saccharin (Aldrich 99%) and 0.11 mol of P_2S_5 (Merck) under an N_2 atmosphere, according to the procedure described by Meadow and Cavagnol [12]. The reaction mixture was extracted with benzene, and the crude orange-yellow product was recrystallized from this solvent. Its purity was confirmed by a sharp melting point ($181 - 182^\circ\text{C}$) and by IR and Raman spectra [11].

The adduct was obtained by dissolution of 1.0 mmol of thiosaccharin in 3 mL of pyridine. The solution was left to evaporate in air, and after a few days small dark-yellow

Table 2. Crystal data and details of the structure refinement of $[\text{HNC}_5\text{H}_5]^+ [(\text{tsac})(\text{Htsac})]^-$.

Formula	$\text{C}_{19}\text{H}_{15}\text{N}_3\text{O}_4\text{S}_4$
M_r	477.58
Crystal system	triclinic
Space group	$P\bar{1}$ (no. 2)
a , Å	8.637(1)
b , Å	8.785(2)
c , Å	15.133(2)
α , deg	74.81(1)
β , deg	84.34(1)
γ , deg	69.98(1)
Volume, Å ³	1041.1(3)
D_c , g cm ⁻³	1.523
Z	2
$F(000)$, e	492
θ range for data collection	3.03–67.94
hkl ranges	$\pm 10, \pm 10, +18$
Reflections collected	3592
Independent reflections	3436
R_{int}	0.069
Observed reflections [$I \geq 2\sigma(I)$]	3004
Data/parameters	3436/271
Goodness-of-fit on F^2	1.085
Final $R1/wR2$ indices [$I \geq 2\sigma(I)$]	0.043/0.117
Final $R1/wR2$ indices (all data)	0.051/0.126
Largest diff. peak/hole, e Å ⁻³	0.28/–0.37

crystals were deposited. They were recrystallized twice from methanol. After slow evaporation of the solvent some crystals adequate for crystallographic studies could be selected under the microscope.

Crystal structure determination

Measurements were performed at 296(2) K with an Enraf-Nonius CAD-4 diffractometer employing graphite-

monochromated $\text{CuK}\alpha$ radiation ($\lambda = 1.54184$ Å). A yellow prismatic crystal of dimensions $0.28 \times 0.24 \times 0.16$ mm³ was used. Intensity data were corrected for Lorentz and polarization effects as well as for absorption (PLATON [8]). The unit cell dimensions were obtained by least-squares refinement of the angular settings for 25 reflections in the range $13.86 < \theta < 46.89^\circ$. Crystal data, collection procedures and refinement results are summarized in Table 2. All hydrogen atoms could be located in a Fourier difference map. However, they were subsequently placed in idealized geometrical positions and refined with a riding model. The final molecular model was obtained by anisotropic full-matrix least-squares refinement of the non-hydrogen atoms. Programs used were CAD-4 EXPRESS [13], XCAD4 [14], and SHELXS-97 [15], for data collection, data reduction and correction and structure solution, respectively, and SHELXL-97 [16] for structure refinement.

CCDC 679551 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Spectroscopic measurements

The infrared spectra of the compound were recorded on KBr pellets in the spectral range $4000 - 400$ cm⁻¹ on a FTIR Bruker IFS 66 spectrophotometer.

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