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Crystal structure of 2-(3-((carbamimidoylthio)methyl)benzyl)isothiuronium hexafluorophosphate monohydrate, $C_{10}H_{17}F_6N_4OPS_2$

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Abstract

$C_{10}H_{17}F_6N_4OPS_2$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 8.7848(9)$ Å, $b = 9.8894(11)$ Å, $c = 18.8020(19)$ Å, $V = 1633.4(3)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0348$, $wR_{ref}(F^2) = 0.0943$, $T = 150$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colorless prism
Size	$0.48 \times 0.36 \times 0.32$ mm
Wavelength:	Cu K α radiation (1.5418 Å)
μ :	4.58 mm ⁻¹
Diffractometer, scan mode:	Xcalibur, ω
θ_{max} , completeness:	77.6°, 98%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	7351, 3391, 0.029
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 3211
$N(param)_{refined}$:	253
Programs:	CrysAlis ^{PRO} [1], SUPERFLIP [2], JANA2006 [3], Diamond [4]

Source of material

The solution of thiourea (0.63 g, 8.33 mmol) in ethanol (50 mL) was heated to reflux. To the boiling solution 1,3-bis(bromomethyl)benzene (1.00 g, 3.78 mmol) was added. The heating continued for 50 min, then the mixture was allowed to cool to room temperature. The resulting crystals were filtered off, washed with hexane and dried under reduced pressure resulting in yield of 1.21 g (77%) of

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
S1	0.68233 (7)	0.02355 (6)	0.02797 (3)	0.02315 (16)
S2	1.08443 (7)	0.35220 (7)	0.30822 (3)	0.02634 (17)
P1	0.44985 (7)	0.04417 (6)	0.35013 (3)	0.02075 (16)
F1	0.4046 (2)	−0.07775 (15)	0.40820 (8)	0.0245 (4)
F2	0.49953 (18)	0.16838 (15)	0.29149 (8)	0.0236 (4)
F3	0.5231 (3)	−0.07154 (18)	0.29424 (9)	0.0376 (6)
F4	0.3808 (2)	0.16360 (16)	0.40572 (9)	0.0325 (5)
F5	0.28036 (19)	0.02906 (19)	0.31083 (10)	0.0333 (5)
F6	0.6220 (2)	0.0626 (2)	0.38972 (11)	0.0393 (6)
O1w	0.1158 (3)	0.1882 (3)	0.48849 (13)	0.0422 (8)
N1	0.5656 (3)	−0.0702 (2)	0.14606 (12)	0.0236 (6)
N2	0.5892 (3)	0.1602 (2)	0.14368 (11)	0.0235 (6)
N3	0.8935 (3)	0.2055 (3)	0.37975 (14)	0.0314 (7)
N4	0.7897 (3)	0.2990 (3)	0.27966 (13)	0.0299 (7)
C1	0.9371 (3)	0.1791 (3)	0.06753 (12)	0.0210 (6)
C2	0.9468 (3)	0.2859 (3)	0.11568 (13)	0.0223 (6)
C3	1.0685 (3)	0.2927 (3)	0.16315 (13)	0.0226 (6)
C4	1.1820 (3)	0.1950 (3)	0.16169 (14)	0.0261 (7)
C5	1.1732 (3)	0.0912 (3)	0.11283 (14)	0.0267 (7)
C6	1.0507 (3)	0.0810 (3)	0.06642 (13)	0.0242 (7)
C7	0.8037 (3)	0.1722 (3)	0.01672 (12)	0.0223 (6)
C8	0.6073 (3)	0.0417 (2)	0.11314 (12)	0.0177 (6)
C9	1.0760 (3)	0.4082 (3)	0.21625 (14)	0.0254 (7)
C10	0.9061 (3)	0.2804 (3)	0.32287 (13)	0.0236 (7)
H1c2	0.869709	0.354723	0.116168	0.0268 [*]
H1c4	1.265869	0.1997	0.194353	0.0314 [*]
H1c5	1.252926	0.024966	0.110895	0.0321 [*]
H1c6	1.044436	0.006604	0.033736	0.029 [*]
H1c7	0.840382	0.175638	−0.03135	0.0268 [*]
H2c7	0.743373	0.252599	0.02132	0.0268 [*]
H1c9	0.989495	0.466288	0.209874	0.0305 [*]
H2c9	1.162874	0.46384	0.206	0.0305 [*]
H1n1 ^a	0.541 (6)	−0.065 (6)	0.1903 (8)	0.0283 [*]
H2n1 ^b	0.587 (6)	−0.146 (3)	0.126 (2)	0.0283 [*]
H1n2 ^c	0.549 (4)	0.169 (4)	0.1851 (9)	0.0282 [*]
H2n2	0.593 (5)	0.234 (2)	0.1195 (17)	0.0282 [*]
H1n3	0.806 (2)	0.169 (4)	0.386 (2)	0.0377 [*]
H2n3 ^d	0.972 (3)	0.199 (5)	0.407 (2)	0.0377 [*]
H1n4 ^e	0.704 (3)	0.266 (5)	0.293 (2)	0.0359 [*]
H2n4 ^f	0.792 (6)	0.362 (3)	0.2482 (19)	0.0359 [*]
H1o1w	0.135 (6)	0.253 (3)	0.514 (2)	0.0506 [*]
H2o1w	0.195 (3)	0.168 (5)	0.468 (2)	0.0506 [*]

^aOccupancy: 0.70(7), ^bOccupancy: 0.76(7), ^cOccupancy: 0.96(7),^dOccupancy: 0.89(7), ^eOccupancy: 0.85(8), ^fOccupancy: 0.85(16).

2,2'-(1,3-phenylenebis(methylene))diisothiuronium bromide. The reaction product was dissolved in water and mixed with water solution of equimolar amount of silver hexafluorophosphate, the resulting AgBr was filtered off. The filtrate was allowed to slowly evaporate, forming the single crystals of the title compound.

Experimental details

H atoms bonded to C were placed in calculated positions, while H atoms bonded to N and O were refined with restrained bond lengths (N—H = 0.86 Å, O—H = 0.82 Å). In both cases the *U*_{iso}(H) was kept at 1.2 *U*_{eq}(C, N, O). The H atoms bonded to N atoms of S-alkylthiourea and isothiuronium groups are disordered with only H2n2 and H1n3 fully localized. Occupancies of remaining H atoms were refined with a sum constrained to 5 to keep the electroneutrality of the structure.

Comment

The isothiuronium salts are used for anion recognition by charge-assisted hydrogen bonds [5]. Along with isoselenouronium salts they were recently studied for cytostatic activity, achieving promising results [6].

The asymmetric unit of the crystal structure of the title compound, consisting of one water molecule, one hexafluorophosphate anion and one 2-(3-((carbamimidoylthio)methyl)benzyl)isothiuronium cation is depicted in the figure. Due to the hydrogen disorder the S-alkylthiourea and isothiuronium group are indistinguishable; therefore, they will be referred to as isothiuronium groups. The isothiuronium groups were found to be in a pincer-like arrangement, with C(ar)—C(me)—S—C(iso) torsion angles at 63.5(2) and −67.8(2)° for groups bearing S1 and S2 respectively. The isothiuronium groups are slightly tilted away from the benzene core, with S1—C8—N2 and S2—C10—N4 at 122.64(19) and 122.9(2)° respectively, while S1—C8—N1 and S2—C10—N3 angles are at 116.72(18)° and 115.9(2)° respectively. These distortions are probably caused by steric effects. The isothiuronium groups form seven N—H ... F and one N—H ... O hydrogen bonds. The H1n1, H1n2, H1n3 and H1n4 atoms form hydrogen bonds with the same hexafluorophosphate anion in a pincer-like arrangement. The crystal water molecule forms two O—H ... F hydrogen bonds, one of them being significantly weaker with H ... A distance of 2.57(4) Å.

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