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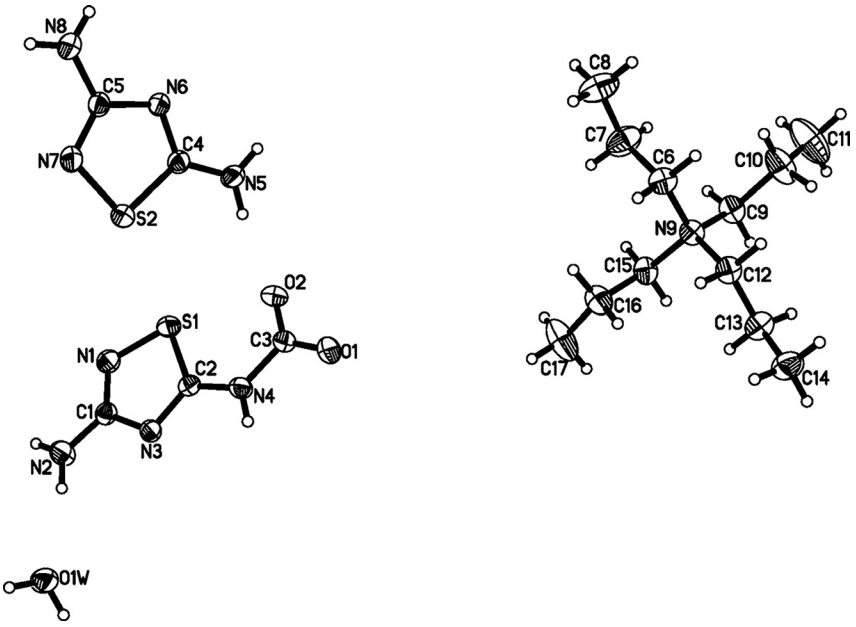
Crystal structure of tetrapropylammonium-1,3,5-thiadiazole-5-amido-2-carbamate – 1,2,4-thiadiazole-3,5-diamine – water (1/1/1), $C_{17}H_{37}N_9O_3S_2$



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Abstract

$C_{17}H_{37}N_9O_3S_2$, monoclinic, $P2_1/c$ (no. 14), a = 8.8492(13) Å, b = 17.285(3) Å, c = 16.810(3) Å, β = 93.493(2)°, V = 2566.4(7) Å^3, Z = 4, $R_{gt}(F)$ = 0.0395, $wR_{ref}(F^2)$ = 0.1277, T = 296(2) K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.50 × 0.20 × 0.20 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.24 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	25.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	12,815, 4511, 0.027
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 3774
$N(param)_{refined}$:	286
Programs:	Bruker [1], SHELX [2, 3]

Source of materials

Amidinothiourea and tetrapropylammonium hydroxide (25% aqueous solution) were mixed in a molar ratio of 1:2. The mixture was dissolved in a minimum amount of ethanol and water to form the related mixture, then the mixture was vigorously stirred for about 1 h. Subsequently the clean solution was set aside to allow it slow evaporation at room temperature. Colorless block crystals were obtained about 10 days later. It can be concluded that some amidinothiourea.

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

Atom	x	Y	z	U_{iso}*/U_{eq}
S1	0.12243 (6)	0.17443 (3)	0.59153 (3)	0.04788 (17)
C1	0.1383 (2)	0.10176 (10)	0.46849 (11)	0.0414 (4)
N1	0.07948 (19)	0.09445 (9)	0.53823 (10)	0.0506 (4)
O1	0.37108 (19)	0.39474 (8)	0.57551 (9)	0.0631 (4)
O1W	0.2481 (2)	0.04833 (11)	0.24913 (10)	0.0709 (5)
H1WA	0.312 (3)	0.0115 (13)	0.2426 (16)	0.106*
H1WB	0.244 (3)	0.0757 (15)	0.2056 (11)	0.106*
S2	0.43503 (6)	0.13059 (3)	0.73061 (3)	0.05315 (18)
C2	0.21949 (19)	0.21342 (10)	0.51537 (10)	0.0386 (4)
N2	0.1206 (2)	0.04674 (10)	0.41115 (11)	0.0592 (5)
H2A	0.0697	0.0055	0.4198	0.071*
H2B	0.1603	0.0531	0.3662	0.071*
O2	0.21952 (19)	0.31527 (9)	0.64117 (8)	0.0597 (4)
C3	0.2935 (2)	0.33514 (11)	0.58270 (11)	0.0465 (5)
N3	0.21863 (17)	0.16771 (8)	0.45213 (9)	0.0419 (4)
C4	0.3784 (2)	0.19067 (10)	0.80634 (11)	0.0431 (4)
N4	0.28868 (19)	0.28350 (9)	0.51791 (9)	0.0484 (4)
H4A	0.3335	0.2976	0.4763	0.058*
C5	0.5103 (2)	0.09813 (10)	0.86760 (11)	0.0428 (4)
N5	0.2969 (2)	0.25515 (10)	0.79488 (10)	0.0575 (5)
H5A	0.2740	0.2827	0.8350	0.069*
H5B	0.2674	0.2692	0.7474	0.069*
N6	0.42830 (18)	0.16483 (9)	0.87695 (9)	0.0432 (4)
C6	0.3234 (2)	0.80349 (13)	0.82371 (13)	0.0562 (5)
H6A	0.3909	0.7693	0.7969	0.067*
H6B	0.3858	0.8387	0.8564	0.067*
N7	0.5300 (2)	0.07139 (9)	0.79536 (10)	0.0506 (4)
C7	0.2309 (3)	0.75532 (19)	0.87778 (17)	0.0858 (8)
H7A	0.1589	0.7885	0.9026	0.103*
H7B	0.1740	0.7171	0.8461	0.103*
N8	0.5714 (2)	0.06313 (10)	0.93440 (10)	0.0580 (5)
H8D	0.6251	0.0220	0.9306	0.070*
H8E	0.5563	0.0821	0.9805	0.070*
C8	0.3265 (4)	0.7150 (2)	0.94119 (18)	0.1016 (10)
H8A	0.2629	0.6853	0.9739	0.152*
H8B	0.3965	0.6813	0.9170	0.152*
H8C	0.3814	0.7526	0.9735	0.152*
N9	0.23328 (16)	0.85037 (10)	0.76111 (10)	0.0474 (4)
C9	0.1309 (2)	0.90868 (13)	0.79916 (14)	0.0577 (5)
H9A	0.0803	0.9392	0.7571	0.069*
H9B	0.0535	0.8805	0.8256	0.069*
C10	0.2082 (3)	0.96331 (18)	0.85885 (19)	0.0910 (9)
H10A	0.2704	0.9335	0.8972	0.109*
H10B	0.2746	0.9974	0.8312	0.109*
C11	0.1029 (5)	1.0096 (3)	0.9010 (3)	0.1485 (18)
H11A	0.1580	1.0431	0.9379	0.223*
H11B	0.0424	1.0402	0.8635	0.223*
H11C	0.0383	0.9763	0.9295	0.223*
C12	0.3501 (2)	0.89099 (13)	0.71169 (13)	0.0519 (5)
H12A	0.4115	0.9243	0.7470	0.062*
H12B	0.4166	0.8518	0.6917	0.062*
C13	0.2889 (3)	0.93893 (15)	0.64195 (14)	0.0649 (6)
H13A	0.2363	0.9838	0.6612	0.078*
H13B	0.2173	0.9086	0.6090	0.078*
C14	0.4181 (3)	0.96494 (17)	0.59285 (15)	0.0755 (7)
H14A	0.3786	0.9954	0.5486	0.113*
H14B	0.4881	0.9955	0.6255	0.113*
H14C	0.4692	0.9204	0.5735	0.113*
C15	0.1293 (2)	0.79903 (12)	0.70784 (14)	0.0537 (5)
H15A	0.0557	0.7753	0.7407	0.064*
H15B	0.0741	0.8318	0.6693	0.064*
C16	0.2058 (3)	0.73593 (14)	0.66329 (15)	0.0660 (6)
H16A	0.2512	0.6989	0.7010	0.079*
H16B	0.2859	0.7581	0.6336	0.079*
C17	0.0938 (4)	0.6951 (2)	0.6067 (2)	0.1111 (13)
H17A	0.1446	0.6552	0.5789	0.167*
H17B	0.0153	0.6725	0.6361	0.167*
H17C	0.0500	0.7316	0.5689	0.167*

Comment

1,3,5-Thiadiazole-5-amido-2-carbamate is a derived compound of amidinothiourea, and amidinothiourea is a key pharmaceutical intermediate of famotidine [4]. In 2012, only two inclusion compounds of the carbamate were reported with the existence of the tetrapropylammonium and tetrabutylammonium counter cation [5]. Also, one dihydrate of tetraethylammonium 1,3,5-thiadiazole-5-amido-2-carbamate was reported in 2022 [6]. It can be seen that the crystal structure of tetrapropylammonium 1,3,5-thiadiazole-5-amido-2-carbamate and 1,2,4-thiadiazole-3,5-diamine was not reported until now. As to 1,2,4-thiadiazole-3,5-diamine, it can be analyzed this compound is also a derivative of amidinothiourea under basic conditions, which is just like 1,3,5-thiadiazole-5-amido-2-carbamate. Compared with 1,3,5-thiadiazole-5-amido-2-carbamate, 1,2,4-thiadiazole-3,5-diamine doesn't absorb extra CO_2 to further yield the additional carboxyl group in the concrete structure. In fact, it has been reported that 1,2,4-thiadiazole-3,5-diamine can be synthesized by amidinothiourea with the existence of H_2O_2 [7]. Obviously, 1,2,4-thiadiazole-3,5-diamine can be obtained under different experimental conditions.

In the asymmetric unit of the crystal structure, there exist one tetrapropylammonium, one 1,3,5-thiadiazole-5-amido-2-carbamate, 1,2,4-thiadiazole-3,5-diamine and one water molecule. Analyzing the crystal structure, it can be seen that 1,2,4-thiadiazole-3,5-diamine an 1,3,5-thiadiazole-5-amido-2-carbamate firstly connect with each other to form a hydrogen-bonded dimer by two N–H···N donor hydrogen bonds and one O···H–N acceptor hydrogen bond, then the dimers are further linked with the water molecules by O–H···O and O–H···N contacts to generate a 3D hydrogen-bonded network with rhombic cavities. As to tetrapropylammonium cations, they are regularly accommodated

among the cavities to form the packed crystal structure. The crystal structure of the title compound can be compared with the structure of tetrapropylammonium-1,3,5-thiadiazole-5-amido-2-carbamate and amidinothiourea that reported in 2012 [5]. It is interesting that amidinothiourea and 1,3,5-thiadiazole-5-amido-2-carbamate also link with each other to be a similar dimer, then the dimers are connected by water molecules to form a similar host lattice with rhombic cavities, in which tetrapropylammonium cations are also contained to form the stable structure. Observing the title structure and the reported structure, the prominent difference of the hydrogen-bonded frameworks is the formation of N–H···S hydrogen bonding that only exist in the latter structure. In the title compound, there is no N–H···S contact due to the formation of the heterocycle. Thus, it can be seen that 1,2,4-thiadiazole-3,5-diamine should be very similar with amidinothiourea in their spatial configurations. Compound, and it can yield various derivatives under suitable conditions.

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