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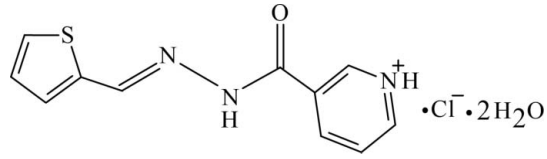

Crystal structure of 3-({[(thiophen-2-yl)-methylidene]hydrazinyl}carbonyl)-pyridinium chloride dihydrate

Thangayyah Chandrasekaran,[a] Mani Suresh,[a] John Josephine Novina,[b] Mohamed Khan Syed Ali Padusha,[a] Gopalsamy Vasuki[c]* and Balasubramani Kasthuri[d]

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In the title compound, $C_{11}H_{10}N_3OS^+\cdot Cl^-\cdot 2H_2O$, the organic cation exhibits a dihedral angle of 21.26 (8)° between the mean planes of the pyridine and thiophene rings, and dihedral angles of 15.11 (9) and 6.49 (9)° between the mean planes of the hydrazide moiety and the pyridine and thiophene rings, respectively. In the crystal, the organic cation, the chloride counter-anion and the two water molecules of crystallization are linked through an intricate hydrogen-bonding network consisting of O—H···O, O—H···N, N—H···Cl, C—H···Cl, C—H···O, N—H···O, O—H···Cl and C—H···S interactions that consolidate a three-dimensional network.

Keywords: crystal structure; pyridinium chloride salt; hydrogen bonding; hydrazone derivatives.

CCDC reference: 1017163

1. Related literature

For structures of related hydrazone derivatives, see: Cheng *et al.* (2008); Jing *et al.* (2007); Novina *et al.* (2013, 2014). For the biological activity of hydrazones, see: Babahan *et al.* (2013); Kaplancikli *et al.* (2012). For graph-set notation, see: Bernstein *et al.* (1995).

2. Experimental

2.1. Crystal data

$C_{11}H_{10}N_3OS^+\cdot Cl^-\cdot 2H_2O$
M_r = 303.76
Triclinic, $P\overline{1}$
a = 7.8781 (7) Å
b = 8.6928 (7) Å
c = 11.0999 (10) Å
α = 67.361 (4)°
β = 78.210 (4)°
γ = 77.119 (4)°
V = 677.97 (10) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.44 mm^{-1}
T = 296 K
0.35 × 0.30 × 0.30 mm

2.2. Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
T_{min} = 0.860, T_{max} = 0.879
5444 measured reflections
3222 independent reflections
2761 reflections with $I > 2\sigma(I)$
R_{int} = 0.016

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.119
S = 1.05
3222 reflections
192 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*N*1···O1W^{i}	0.86	1.80	2.659 (2)	176
N2—H2*N*2···Cl	0.84 (2)	2.59 (2)	3.4011 (14)	163 (2)
O1*W*—H1*O*1···O1	0.87 (2)	2.11 (2)	2.8465 (18)	142 (2)
O1*W*—H1*O*1···N3	0.87 (2)	2.50 (2)	3.2648 (19)	148 (2)
O2*W*—H2*O*2···Cl^{ii}	0.83 (3)	2.41 (3)	3.2305 (18)	171 (3)
O2*W*—H1*O*2···Cl^{iii}	0.85 (2)	2.37 (2)	3.2102 (16)	171 (2)
O1*W*—H2*O*1···O2*W*	0.86 (2)	1.91 (2)	2.764 (2)	170 (3)
C2—H2···S1^{iv}	0.93	2.71	3.6359 (19)	179
C3—H3···Cl	0.93	2.72	3.629 (2)	166
C5—H5···O1^{i}	0.93	2.41	3.207 (2)	143

Symmetry codes: (i) $-x+1, -y+2, -z+2$; (ii) $-x, -y+1, -z+2$; (iii) $x, y+1, z-1$; (iv) $x, y, z+1$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: WM5042).

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supporting information

Acta Cryst. (2014). E**70**, o976–o977 [doi:10.1107/S1600536814017565]

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Thangayyah Chandrasekaran, Mani Suresh, John Josephine Novina, Mohamed Khan Syed Ali Padusha, Gopalsamy Vasuki and Balasubramani Kasthuri

S1. Experimental

Thiophene-2-carboxaldehyde (1.2 ml, 0.01 mol) was added to an ethanolic solution of nicotinicacid hydrazide (1.37 g, 0.01 mol). After the addition was complete, the reaction mixture was stirred thoroughly at 273 K. To this mixture concentrated hydrochloric acid (five drops) was added and stirred. The reaction mixture was kept at this temperature for 30 min. On completion of the reaction, the resulting solid mass was seperated, filtered, dried and washed with diethyl-ether. A pale yellow solid was obtained that was recrystallized from ethanol [yield: 82%].

S2. Refinement

The H atoms of the solvent water molecules and of the hydrazide moiety were located in a difference map and were refined freely. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C—H = 0.93 Å, N—H = 0.86 Å and with U_{iso}(H) = 1.2U_{eq}(C, N).

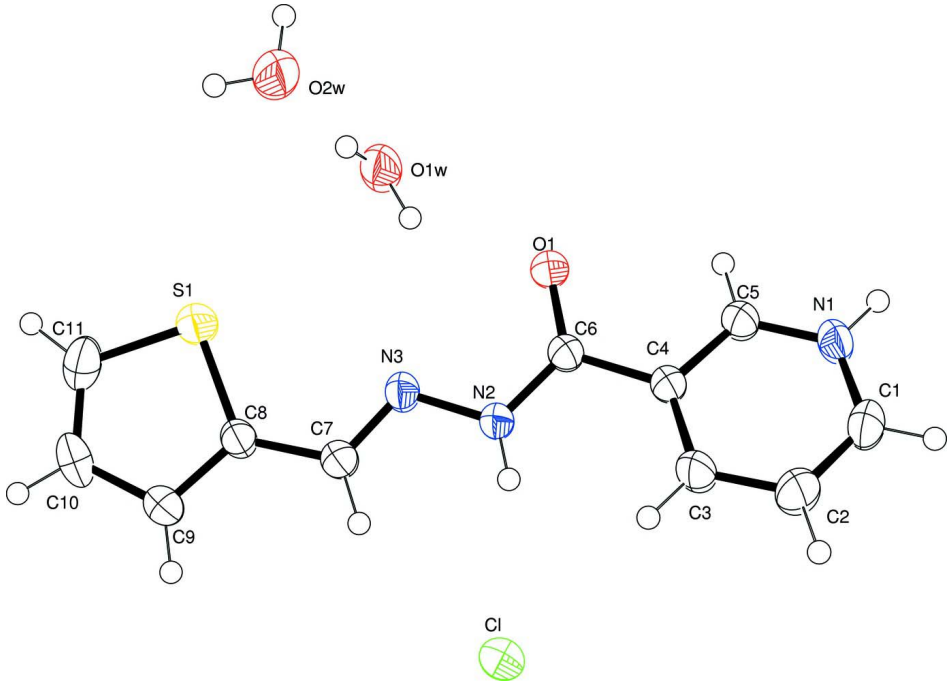

Figure 1

The molecular structure of the title compound, with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

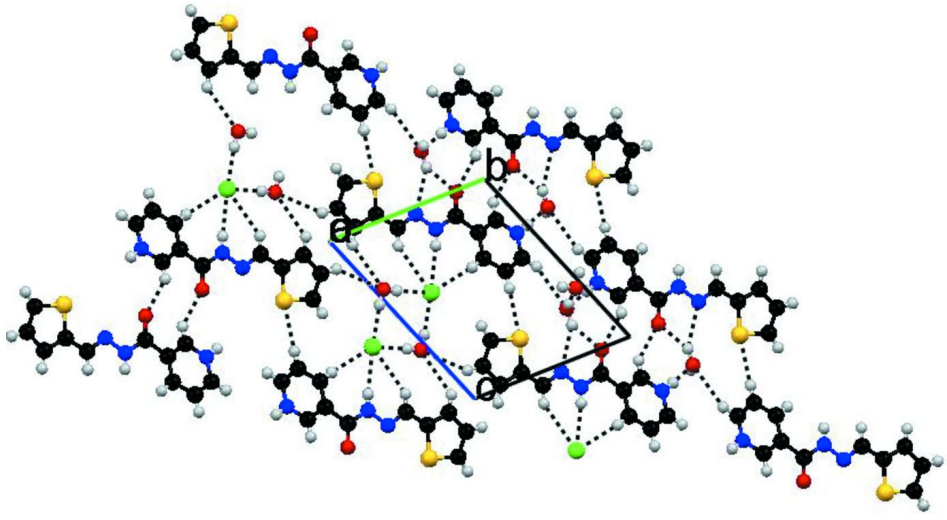

Figure 2

The crystal packing of the title compound viewed along the *a* axis. Hydrogen bonds are shown as dashed lines. $R^4_4(10)$, $R^2_2(10)$, $R^2_1(6)$, $R^2_1(7)$, $R^3_2(8)$ $R^3_3(7)$ and $R^3_3(10)$ ring motifs (Bernstein *et al.*, 1995) are observed in the packing.

3-({[(Thiophen-2-yl)methylidene]hydrazinyl}carbonyl)pyridinium chloride dihydrate

Crystal data

$C_{11}H_{10}N_3OS^+\cdot Cl^-\cdot 2H_2O$
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Triclinic, $P\overline{1}$
Hall symbol: -P 1

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β = 78.210 (4)°
γ = 77.119 (4)°
V = 677.97 (10) Å^3
Z = 2
F(000) = 316

D_x = 1.488 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3509 reflections
θ = 2.6–28.0°
μ = 0.44 mm^{-1}
T = 296 K
Block, pale yellow
0.35 × 0.30 × 0.30 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scan
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
T_{min} = 0.860, T_{max} = 0.879

5444 measured reflections
3222 independent reflections
2761 reflections with $I > 2\sigma(I)$
R_{int} = 0.016
θ_{max} = 28.2°, θ_{min} = 2.6°
h = −9→10
k = −7→11
l = −14→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.119
S = 1.05
3222 reflections
192 parameters
6 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.076P)^2 + 0.1235P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	y	z	U_{iso}*/U_{eq}
S1	0.17836 (6)	0.47295 (5)	0.80609 (4)	0.04223 (14)
Cl	0.17151 (7)	0.25503 (5)	1.42848 (4)	0.05065 (16)
O1	0.38027 (16)	0.80909 (14)	1.00852 (10)	0.0399 (3)
O1W	0.3488 (2)	0.82526 (19)	0.75281 (13)	0.0514 (3)
N2	0.31200 (17)	0.55367 (15)	1.14192 (12)	0.0315 (3)
N3	0.27791 (16)	0.52406 (15)	1.03627 (12)	0.0306 (3)
O2W	0.0187 (2)	0.9549 (2)	0.67510 (14)	0.0640 (4)

N1	0.47813 (17)	0.91856 (17)	1.31029 (13)	0.0367 (3)
H1N1	0.5298	1.0037	1.2922	0.044*
C9	0.1401 (2)	0.18261 (19)	0.98202 (16)	0.0367 (3)
H9	0.1335	0.0925	1.0618	0.044*
C4	0.37426 (18)	0.74005 (17)	1.23659 (14)	0.0287 (3)
C6	0.35574 (18)	0.70370 (17)	1.11885 (13)	0.0284 (3)
C5	0.4561 (2)	0.87569 (19)	1.21193 (15)	0.0329 (3)
H5	0.4964	0.9381	1.1257	0.040*
C7	0.23292 (19)	0.38064 (18)	1.06447 (14)	0.0318 (3)
H7	0.2300	0.3041	1.1506	0.038*
C8	0.18671 (19)	0.33584 (18)	0.96480 (14)	0.0306 (3)
C11	0.1187 (2)	0.3284 (3)	0.76111 (18)	0.0471 (4)
H11	0.0986	0.3481	0.6763	0.057*
C10	0.1041 (2)	0.1815 (2)	0.86327 (19)	0.0466 (4)
H10	0.0732	0.0886	0.8558	0.056*
C3	0.3133 (3)	0.6516 (2)	1.36593 (16)	0.0471 (4)
H3	0.2565	0.5600	1.3860	0.056*
C2	0.3378 (3)	0.7008 (3)	1.46513 (17)	0.0610 (6)
H2	0.2962	0.6429	1.5522	0.073*
C1	0.4229 (3)	0.8340 (2)	1.43523 (17)	0.0481 (4)
H1	0.4421	0.8655	1.5019	0.058*
H2N2	0.298 (3)	0.482 (3)	1.218 (2)	0.057 (6)*
H1O1	0.337 (4)	0.778 (3)	0.8380 (17)	0.086 (9)*
H2O2	−0.019 (4)	0.898 (3)	0.644 (3)	0.093 (10)*
H1O2	0.047 (3)	1.041 (3)	0.610 (2)	0.078 (8)*
H2O1	0.243 (2)	0.854 (3)	0.734 (3)	0.079 (9)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0576 (3)	0.0397 (2)	0.0315 (2)	−0.01844 (18)	−0.00473 (17)	−0.00956 (16)
Cl	0.0716 (3)	0.0443 (3)	0.0392 (2)	−0.0295 (2)	−0.0095 (2)	−0.00611 (18)
O1	0.0609 (7)	0.0349 (5)	0.0264 (5)	−0.0208 (5)	−0.0068 (5)	−0.0060 (4)
O1W	0.0708 (9)	0.0549 (8)	0.0352 (7)	−0.0351 (7)	−0.0011 (6)	−0.0127 (6)
N2	0.0442 (7)	0.0286 (6)	0.0247 (6)	−0.0124 (5)	−0.0048 (5)	−0.0091 (5)
N3	0.0361 (6)	0.0319 (6)	0.0282 (6)	−0.0097 (5)	−0.0034 (5)	−0.0135 (5)
O2W	0.0985 (12)	0.0610 (9)	0.0386 (7)	−0.0414 (8)	−0.0182 (7)	−0.0039 (6)
N1	0.0451 (7)	0.0370 (7)	0.0360 (7)	−0.0189 (6)	−0.0028 (5)	−0.0161 (5)
C9	0.0448 (8)	0.0295 (7)	0.0375 (8)	−0.0108 (6)	−0.0059 (6)	−0.0108 (6)
C4	0.0331 (7)	0.0275 (6)	0.0272 (7)	−0.0086 (5)	−0.0032 (5)	−0.0099 (5)
C6	0.0307 (7)	0.0284 (6)	0.0276 (7)	−0.0080 (5)	−0.0033 (5)	−0.0099 (5)
C5	0.0384 (7)	0.0332 (7)	0.0294 (7)	−0.0140 (6)	−0.0017 (5)	−0.0104 (6)
C7	0.0377 (7)	0.0298 (7)	0.0293 (7)	−0.0087 (5)	−0.0032 (5)	−0.0107 (5)
C8	0.0342 (7)	0.0297 (7)	0.0306 (7)	−0.0096 (5)	−0.0021 (5)	−0.0125 (5)
C11	0.0487 (9)	0.0635 (11)	0.0410 (9)	−0.0144 (8)	−0.0078 (7)	−0.0276 (8)
C10	0.0490 (9)	0.0458 (9)	0.0606 (11)	−0.0173 (7)	−0.0065 (8)	−0.0307 (8)
C3	0.0756 (13)	0.0421 (9)	0.0295 (8)	−0.0334 (9)	0.0031 (7)	−0.0111 (7)
C2	0.1039 (17)	0.0616 (12)	0.0248 (8)	−0.0459 (12)	0.0060 (9)	−0.0126 (8)

C1	0.0703 (12)	0.0516 (10)	0.0336 (8)	−0.0218 (9)	−0.0054 (8)	−0.0214 (7)

Geometric parameters (Å, º)

S1—C11	1.6999 (18)	C9—C10	1.408 (2)
S1—C8	1.7101 (15)	C9—H9	0.9300
Cl—Cl	0.0000 (12)	C4—C5	1.3780 (19)
O1—C6	1.2226 (17)	C4—C3	1.384 (2)
O1W—H1O1	0.868 (17)	C4—C6	1.4985 (19)
O1W—H2O1	0.857 (16)	C5—H5	0.9300
N2—C6	1.3389 (18)	C7—C8	1.438 (2)
N2—N3	1.3804 (17)	C7—H7	0.9300
N2—H2N2	0.83 (2)	C11—C10	1.352 (3)
N3—C7	1.2764 (18)	C11—H11	0.9300
O2W—H2O2	0.837 (17)	C10—H10	0.9300
O2W—H1O2	0.851 (16)	C3—C2	1.386 (2)
N1—C1	1.328 (2)	C3—H3	0.9300
N1—C5	1.3344 (19)	C2—C1	1.364 (3)
N1—H1N1	0.8600	C2—H2	0.9300
C9—C8	1.393 (2)	C1—H1	0.9300
C11—S1—C8	92.07 (8)	N3—C7—C8	120.85 (13)
H1O1—O1W—H2O1	104 (2)	N3—C7—H7	119.6
C6—N2—N3	117.65 (12)	C8—C7—H7	119.6
C6—N2—H2N2	122.4 (16)	C9—C8—C7	126.41 (14)
N3—N2—H2N2	119.8 (16)	C9—C8—S1	111.11 (11)
C7—N3—N2	114.96 (12)	C7—C8—S1	122.47 (11)
H2O2—O2W—H1O2	106 (2)	C10—C11—S1	111.95 (13)
C1—N1—C5	122.12 (13)	C10—C11—H11	124.0
C1—N1—H1N1	118.9	S1—C11—H11	124.0
C5—N1—H1N1	118.9	C11—C10—C9	113.50 (15)
C8—C9—C10	111.34 (14)	C11—C10—H10	123.2
C8—C9—H9	124.3	C9—C10—H10	123.2
C10—C9—H9	124.3	C4—C3—C2	119.31 (15)
C5—C4—C3	118.07 (14)	C4—C3—H3	120.3
C5—C4—C6	116.35 (12)	C2—C3—H3	120.3
C3—C4—C6	125.57 (13)	C1—C2—C3	120.10 (16)
O1—C6—N2	123.36 (13)	C1—C2—H2	120.0
O1—C6—C4	119.87 (12)	C3—C2—H2	120.0
N2—C6—C4	116.77 (12)	N1—C1—C2	119.56 (15)
N1—C5—C4	120.82 (13)	N1—C1—H1	120.2
N1—C5—H5	119.6	C2—C1—H1	120.2
C4—C5—H5	119.6		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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