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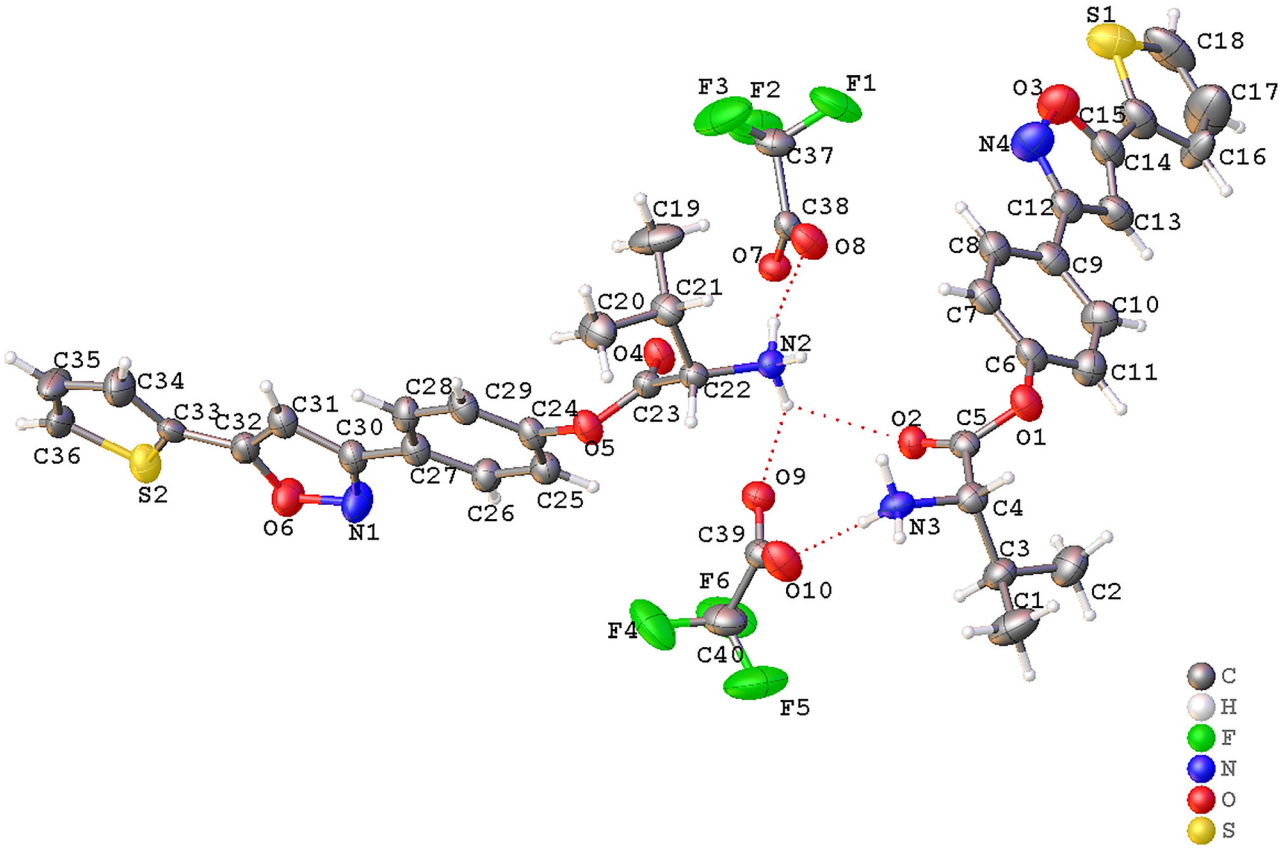
The crystal structure of valinyl-*N*-ium-4-(5-(thiophen-2-yl)isoxazol-3-yl)phenyl trifluoroacetate



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Abstract

$C_{18}H_{18}N_2O_3S{\cdot}C_2HF_3O_2$, monoclinic, $P2_1$ (no. 4), a = 6.0979(2) Å, b = 32.3052(9) Å, c = 11.0805(3) Å, β = 99.5620(10)°, V = 2152.46(11) Å^3, Z = 4, $R_{gt}(F)$ = 0.0570, $wR_{ref}(F^2)$ = 0.1470, T = 200(1) 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:	Colourless block
Size:	0.12 × 0.06 × 0.05 mm
Wavelength:	Ga *K*α radiation (1.34139 Å)
μ:	1.22 mm^{-1}
Diffractometer, scan mode:	Bruker D8 Venture Photon III, φ and ω
θ_{max}, completeness:	57.1°, 99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	62,518, 8248, 0.058
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 6216
$N(param)_{refined}$:	629
Programs:	Bruker [1], Olex2 [2], SHELX [3, 4]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	−0.6370 (14)	0.4383 (3)	0.3581 (7)	0.109 (3)
H1A	−0.661656	0.437693	0.268459	0.164*
H1B	−0.671080	0.465978	0.386058	0.164*
H1C	−0.734077	0.417927	0.388303	0.164*
C2	−0.3363 (13)	0.3856 (2)	0.3607 (7)	0.090 (2)
H2A	−0.407677	0.363856	0.402350	0.134*
H2B	−0.174582	0.381919	0.378000	0.134*
H2C	−0.387911	0.383738	0.272309	0.134*
C3	−0.3967 (10)	0.42789 (18)	0.4068 (5)	0.0646 (14)
H3	−0.301684	0.449019	0.374346	0.077*
C4	−0.3483 (9)	0.43032 (16)	0.5477 (5)	0.0524 (12)
H4	−0.455171	0.412195	0.582555	0.063*
C5	−0.1138 (9)	0.41653 (16)	0.5952 (4)	0.0488 (11)
C6	0.1010 (8)	0.35709 (16)	0.6596 (5)	0.0559 (13)
C7	0.2411 (10)	0.36888 (17)	0.7624 (6)	0.0652 (15)
H7	0.203605	0.391312	0.810548	0.078*
C8	0.4411 (10)	0.34750 (17)	0.7962 (6)	0.0649 (14)
H8	0.541570	0.355743	0.867004	0.078*
C9	0.4933 (9)	0.31451 (18)	0.7273 (6)	0.0618 (14)
C10	0.3475 (10)	0.30325 (19)	0.6235 (6)	0.0700 (16)
H10	0.382456	0.280463	0.575958	0.084*
C11	0.1509 (10)	0.32478 (19)	0.5878 (6)	0.0717 (16)
H11	0.052607	0.317391	0.515284	0.086*
C12	0.6974 (9)	0.29010 (18)	0.7656 (5)	0.0634 (14)
C13	0.7959 (10)	0.25967 (18)	0.6986 (6)	0.0692 (15)
H13	0.745194	0.250445	0.617403	0.083*
C14	0.9774 (10)	0.24685 (19)	0.7762 (7)	0.0735 (17)
C15[a]	1.152 (2)	0.2179 (4)	0.7697 (8)	0.082 (2)
C15A[b]	1.14 (3)	0.217 (4)	0.751 (5)	0.082 (2)
C16[a]	1.1643 (13)	0.1890 (2)	0.6744 (7)	0.077 (2)
H16[a]	1.046981	0.184048	0.608059	0.092*
C16A[b]	1.191 (18)	0.201 (3)	0.639 (4)	0.077 (2)
H16A[b]	1.179360	0.216467	0.564639	0.092*
C17[a]	1.369 (2)	0.1688 (4)	0.6896 (15)	0.149 (5)
H17[a]	1.416212	0.151600	0.629302	0.179*
C17A[b]	1.26 (3)	0.160 (3)	0.654 (6)	0.149 (5)
H17A[b]	1.239493	0.138549	0.594300	0.179*
C18[a]	1.4863 (17)	0.1762 (3)	0.7956 (12)	0.116 (4)
H18[a]	1.622520	0.162513	0.825373	0.139*
C18A[b]	1.37 (2)	0.156 (3)	0.766 (6)	0.116 (4)
H18A[b]	1.501902	0.139356	0.789229	0.139*
N3	−0.3692 (7)	0.47384 (13)	0.5904 (4)	0.0520 (10)
H3A	−0.268109	0.490138	0.561168	0.062*
H3B	−0.343279	0.474510	0.673652	0.062*
H3C	−0.508780	0.483351	0.562320	0.062*
N4	0.8100 (9)	0.2950 (2)	0.8760 (6)	0.0870 (16)
O1	−0.1092 (6)	0.37611 (11)	0.6254 (4)	0.0617 (9)
O2	0.0470 (6)	0.43798 (10)	0.5979 (3)	0.0538 (8)
O3	0.9896 (8)	0.26727 (16)	0.8848 (5)	0.0893 (13)
S1[a]	1.3751 (4)	0.21190 (8)	0.8743 (2)	0.0994 (8)
S1A[b]	1.250 (5)	0.1846 (11)	0.860 (3)	0.0994 (8)
C19	0.3839 (14)	0.5363 (3)	1.0528 (6)	0.106 (3)
H19A	0.510411	0.552984	1.037077	0.160*
H19B	0.413496	0.507000	1.039178	0.160*
H19C	0.362111	0.540329	1.137631	0.160*
C20	0.1124 (12)	0.59379 (19)	0.9909 (6)	0.0787 (18)
H20A	0.084832	0.596241	1.075296	0.118*
H20B	−0.022641	0.601265	0.934157	0.118*
H20C	0.233634	0.612453	0.978879	0.118*
C21	0.1766 (10)	0.54957 (17)	0.9670 (5)	0.0603 (13)
H21	0.052532	0.531409	0.984104	0.072*
C22	0.1968 (8)	0.54331 (14)	0.8300 (4)	0.0455 (11)
H22	0.067792	0.557170	0.778120	0.055*
C23	0.4082 (8)	0.56117 (14)	0.7993 (4)	0.0461 (11)
C24	0.5678 (8)	0.62515 (15)	0.7549 (5)	0.0514 (12)
C25	0.6822 (9)	0.61773 (16)	0.6608 (5)	0.0568 (13)
H25	0.641487	0.595571	0.605229	0.068*
C26	0.8593 (9)	0.64353 (17)	0.6489 (5)	0.0567 (13)
H26	0.942413	0.638636	0.585001	0.068*
C27	0.9177 (8)	0.67652 (15)	0.7292 (5)	0.0546 (12)
C28	0.7980 (9)	0.68237 (16)	0.8233 (5)	0.0583 (13)
H28	0.838036	0.704256	0.879907	0.070*
C29	0.6210 (9)	0.65700 (16)	0.8367 (5)	0.0580 (13)
H29	0.538072	0.661491	0.900879	0.070*
C30	1.1037 (9)	0.70433 (16)	0.7172 (5)	0.0566 (13)
C31	1.2100 (9)	0.73339 (16)	0.8031 (5)	0.0567 (13)
H31	1.178360	0.738967	0.882579	0.068*
C32	1.3649 (9)	0.75133 (16)	0.7479 (5)	0.0569 (13)
C33[c]	1.536 (2)	0.7819 (4)	0.7905 (9)	0.053 (2)
C33A[d]	1.522 (10)	0.7853 (18)	0.764 (4)	0.053 (2)
C34[c]	1.555 (7)	0.8040 (13)	0.898 (3)	0.088 (4)
H34[c]	1.459063	0.801682	0.956729	0.105*
C34A[d]	1.665 (6)	0.8005 (13)	0.690 (4)	0.0685 (8)
H34A[d]	1.647914	0.801054	0.603230	0.082*
C35[c]	1.744 (2)	0.8314 (4)	0.9050 (8)	0.088 (3)
H35[c]	1.785017	0.850075	0.971227	0.105*
C35A[d]	1.850 (6)	0.8157 (14)	0.781 (4)	0.068 (2)
H35A[d]	2.002047	0.812142	0.774832	0.082*
C36[c]	1.8582 (16)	0.8286 (3)	0.8104 (9)	0.068 (2)
H36[c]	1.986900	0.844258	0.802902	0.082*
C36A[d]	1.776 (9)	0.8354 (18)	0.875 (4)	0.088 (3)
H36A[d]	1.842978	0.858810	0.918084	0.105*
N1	1.1896 (8)	0.70468 (17)	0.6161 (5)	0.0732 (14)
N2	0.1935 (6)	0.49881 (12)	0.7985 (3)	0.0452 (9)
H2D	0.193163	0.495897	0.716751	0.054*
H2E	0.069003	0.486892	0.818347	0.054*
H2F	0.316106	0.486247	0.840876	0.054*

Table 2: (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
O4	0.5799 (6)	0.54281 (10)	0.8032 (3)	0.0584 (9)
O5	0.3799 (5)	0.60135 (10)	0.7698 (3)	0.0551 (9)
O6	1.3588 (7)	0.73483 (13)	0.6341 (4)	0.0720 (11)
S2[c]	1.7380 (3)	0.79261 (7)	0.7063 (2)	0.0685 (8)
S2A[d]	1.541 (7)	0.8101 (13)	0.902 (3)	0.088 (4)
C37	0.8652 (11)	0.4357 (2)	1.0357 (5)	0.0684 (16)
C38	0.7152 (8)	0.44687 (14)	0.9148 (4)	0.0445 (10)
F1	0.8156 (8)	0.39861 (15)	1.0728 (5)	0.1183 (16)
F2	1.0775 (6)	0.43516 (17)	1.0297 (4)	0.1082 (15)
F3	0.8407 (10)	0.4616 (2)	1.1223 (4)	0.146 (2)
O7	0.8143 (5)	0.45581 (11)	0.8292 (3)	0.0523 (8)
O8	0.5164 (6)	0.44606 (12)	0.9170 (4)	0.0676 (10)
C39	0.0802 (9)	0.53702 (15)	0.4982 (5)	0.0510 (12)
C40[e]	0.137 (3)	0.5637 (6)	0.3935 (16)	0.088 (3)
C40A[f]	0.104 (4)	0.5605 (7)	0.3812 (18)	0.088 (3)
F4[e]	0.168 (3)	0.6030 (3)	0.4273 (15)	0.128 (6)
F4A[f]	0.315 (4)	0.5707 (10)	0.380 (2)	0.156 (12)
F5[e]	−0.016 (3)	0.5623 (9)	0.2970 (15)	0.169 (8)
F5A[f]	−0.025 (5)	0.5927 (6)	0.3650 (18)	0.153 (9)
F6[e]	0.323 (3)	0.5543 (6)	0.3565 (15)	0.122 (7)
F6A[f]	0.043 (4)	0.5376 (6)	0.2848 (14)	0.133 (7)
O9	0.2496 (6)	0.52251 (11)	0.5625 (3)	0.0568 (9)
O10	−0.1136 (7)	0.53458 (13)	0.5136 (5)	0.0803 (12)

[a]Occupancy: 0.932 (4), [b]occupancy: 0.068 (4), [c]occupancy: 0.797 (8), [d]occupancy: 0.203 (8), [e]occupancy: 0.55 (2), [f]occupancy: 0.45 (2).

1 Source of materials

At first, 4-(5-(cyclopenta-1,3-dien-1-yl)isoxazol-3-yl)phenol (0.25 g, 1 mmol) and 2-amino-3-methylbutyric acid (0.38 g, 2 mmol) were stirred well with 10 mL of dichloromethane at room temperature for 8 h. After the reaction, 20 mL of water was added into the resulting mixture. The mixture was extracted with dichloromethane (10 mL × 3). Afterwards, the extract was washed with saturated sodium chloride solution, dried over anhydrous $MgSO_4$ and concentrated to obtain the crude product. The crude product was purified by recrystallization using ethyl acetate to obtain the target compound 4-(5-(thiophen-2-yl) isoxazol-3-yl)phenyl valinate. Finally, the target compound (20.0 mg, 0.06 mmol) was dissolved in the mixed solvent of acetone (5 mL) and trifluoroacetic acid (0.01 mL). The solution was filtered and placed in a vial. The crystals were obtained by slow evaporation of the solution at 26 °C within 7 days.

2 Experimental details

Using Olex2 [2], the structure was solved with the XM [3] structure solution program using Dual Space and refined with the XL [4] refinement package.

3 Comment

Isoxazole compounds occupy a significant position in the pesticide market. They have excellent biological activities in weeding [5], pest control [6], and antifungal [7]. Meanwhile, researchers were also conducting in-depth studies on the structures of isoxazoles. For instance, the X-ray crystal structures of copper (II)-isoxazole binary complexes [8], the structures of fluorescent biaryl-substituted isoxazoles [9], the structures of 2-nitroimidazole-3,5-disubstituted isoxazole compounds based on benznidazole [10] and so on. However, there are few studies on the isoxazole structure containing valine molecules.

The asymmetric unit of the title structure contains two organic cations and two trifluoroacetic acid molecules. It indicates that the hydrogen bonding interactions play an important role in the crystal structure. Two cations firstly interact with each other to form a dimer by a pair of N–H···O [N2–H2d···O2, length 2.989(5) Å, angle 124.9°] hydrogen bonds. At the same time, one cation and one trifluoroacetic acid link with each other by N–H···O [N3–H3a···O10, length 2.728(6) Å, angle 164.1°]. The other cations also link with each other by N–H···O [N2–H2d···O9, length 2.799(5) Å, angle 146.8°], forming a stable triangular area finally generating a 2-dimensional hydrogen-bonded layer. All bond lengths and angles are within a reasonable range [11].

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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