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2-[5-(Pyridin-2-yl)-1,3,4-thiadiazol-2-yl]pyridin-1-ium perchlorate

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Keywords: crystal structure; pyridine; pyridinium; thiadiazole; hydrogen bonding; offset π–π interactions.

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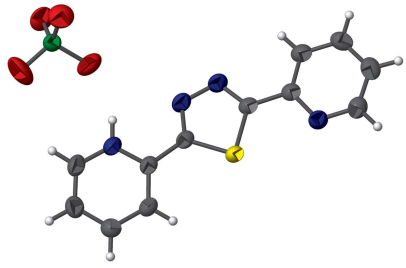
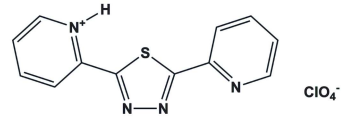
Structural data: full structural data are available from iucrdata.iucr.org

The cation of the title molecular salt, $C_{12}H_9N_4S^+\cdot ClO_4^-$, is approximately planar, with the pyridine and pyridinium rings being inclined to the central thiadiazole ring by 6.51 (9) and 9.13 (9)°, respectively. The dihedral angle between the pyridine and pyridinium rings is 12.91 (10)°. In the crystal, the cations are linked by N—H···O and C—H···O hydrogen bonds, involving the perchlorate anion, forming chains propagating along the [100] direction. The chains are linked by weak offset π–π interactions [inter-centroid distance = 3.586 (1) Å], forming layers parallel to the *ab* plane.

3D view



Chemical scheme



Structure description

Transition metal complexes with the ligand 2,5-bis(pyridin-2-yl)-1,3,4-thiadiazole (**L**) have attracted considerable attention owing to their magnetic properties (Klingele *et al.*, 2010) and biological activity (Zine *et al.*, 2016). Indeed, the ligand (**L**) can coordinate to different metal ions in many modes (Bentiss *et al.*, 2002, 2011; Ahmed *et al.*, 2015; Laachir *et al.*, 2013, 2015*a*,*b*). However, we observed the formation of the title compound with the same ligand after the addition of perchloric acid, as a result of the proton donor-acceptor reaction between perchloric acid and 2,5-bis(pyridin-2-yl)-1,3,4-thiadiazole (**L**). In this case, no metallic salt was used.

The structure of the title molecular salt is shown in Fig. 1. The cation is almost planar with the pyridine (N1/C1–C5) and pyridinium (N4/C8–C12) rings being inclined to the central thiadiazole (S1/N2/N3/C6/C7) ring by 6.51 (9) and 9.13 (9)°, respectively. The dihedral angle between the pyridine and pyridinium rings is 12.91 (10)°.

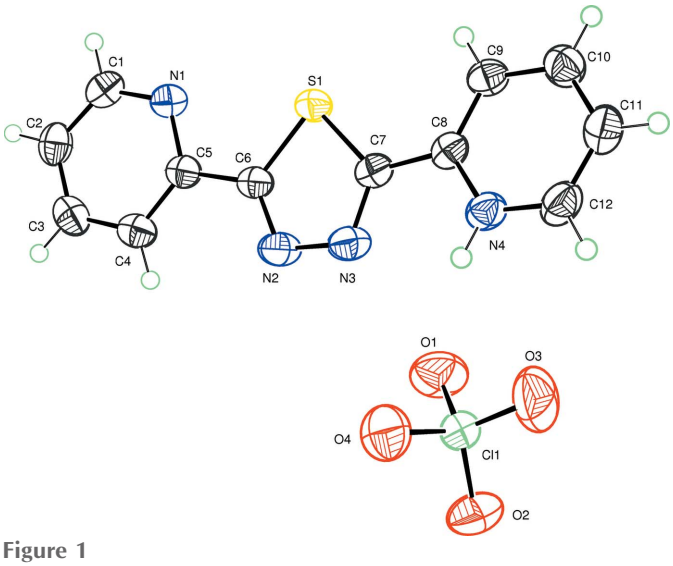


Figure 1
The molecular structure of the title molecular salt, with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

In the crystal, the cations are linked by N—H···O and C—H···O hydrogen bonds, involving the perchlorate anion, forming chains propagating along the [100] direction; Table 1 and Fig. 2. The chains are linked by weak offset π–π interactions [$Cg2\cdots Cg1^{i}$ = 3.586 (1) Å; $Cg2$ and $Cg1$ are the centroids of the N1/C1–C5 and S1/N2/N3/C6/C7 rings, respectively; interplanar distance 3.4952 (8) Å; slippage 0.734 Å; α = 6.51 (9)°; symmetry code: (i) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$], forming layers parallel to the *ab* plane (Fig. 2).

Synthesis and crystallization

The 2,5-bis(pyridin-2-yl)-1,3,4-thiadiazole ligand (**L**) was synthesized as described previously (Lebrini *et al.*, 2005). To a solution of **L** (24 mg, 0.1 mmol) in EtOH (10 ml) was added dropwise $HClO_4$ (1 ml, 1 mol/l) with stirring at 318 K. The resulting solution was filtered after 2 h and allowed to stand in air for the solvent to evaporate slowly. After one month, colourless block-like crystals of the title compound were isolated and dried under vacuum (yield 40%, m.p. > 543 K). Elemental Analysis for $C_{12}H_9N_4SClO_4$. Calculated: C 42.30; H 2.66; N 16.44; S 9.41%, found: C 42.86; H 2.70; N 16.54; S 9.87%.

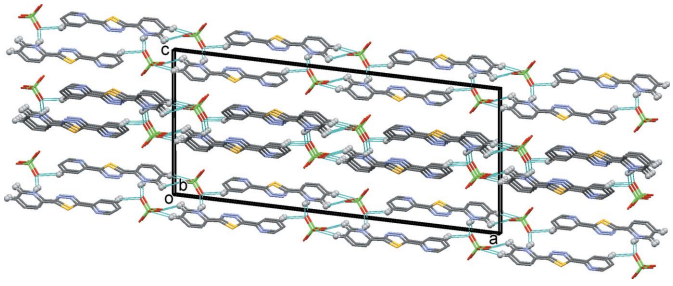


Figure 2
A view along the *b* axis of the crystal packing of the title molecular salt. The hydrogen bonds shown as dashed lines (see Table 1).

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4A···O1	0.86	2.01	2.820 (2)	157
C11—H11···O2^{i}	0.93	2.49	3.228 (3)	136
C12—H12···O3^{i}	0.93	2.58	3.268 (3)	131

Symmetry code: (i) $-x+1, -y+1, -z+1$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{12}H_9N_4S^{+}\cdot ClO_4^{-}$
M_r	340.74
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	296
a, *b*, *c* (Å)	33.5367 (15), 5.5506 (2), 14.7248 (7)
β (°)	96.873 (2)
V (Å^3)	2721.3 (2)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.46
Crystal size (mm)	0.31 × 0.26 × 0.24
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.672, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	50011, 3824, 2916
R_{int}	0.052
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.694
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.111, 1.03
No. of reflections	3824
No. of parameters	200
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.64, −0.36

Computer programs: *APEX2* and *SAINT* (Bruker, 2009), *SHELXT2014* (Sheldrick, 2015*a*), *ORTEP-3 for Windows* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2008), *SHELXL2014* (Sheldrick, 2015*b*) and *publCIF* (Westrip, 2010).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

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full crystallographic data

IUCrData (2017). **2**, x170465 [https://doi.org/10.1107/S2414314617004655]

2-[5-(Pyridin-2-yl)-1,3,4-thiadiazol-2-yl]pyridin-1-ium perchlorate

Abdelhakim Laachir, Fouad Bentiss, Salaheddine Guesmi, Mohamed Saadi and Lahcen El Ammari

2-[5-(Pyridin-2-yl)-1,3,4-thiadiazol-2-yl]pyridin-1-ium perchlorate

Crystal data

$C_{12}H_9N_4S^+\cdot ClO_4^-$
M_r = 340.74
Monoclinic, $C2/c$
a = 33.5367 (15) Å
b = 5.5506 (2) Å
c = 14.7248 (7) Å
β = 96.873 (2)°
V = 2721.3 (2) Å^3
Z = 8
$F(000)$ = 1392
D_x = 1.663 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3824 reflections
θ = 2.5–29.6°
μ = 0.46 mm^{-1}
T = 296 K
Block, colourless
0.31 × 0.26 × 0.24 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.672, T_{max} = 0.747
50011 measured reflections
3824 independent reflections
2916 reflections with $I > 2\sigma(I)$
R_{int} = 0.052
θ_{max} = 29.6°, θ_{min} = 2.5°
h = −46→46
k = −7→7
l = −20→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.111
S = 1.03
3824 reflections
200 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0492P)^2 + 3.1258P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.64 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}
Extinction correction: (SHELXL2014; Sheldrick, 2015b), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00101 (19)

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.18047 (6)	0.1642 (4)	0.65832 (15)	0.0455 (5)
H1	0.1681	0.0341	0.6833	0.055*
C2	0.15657 (6)	0.3515 (4)	0.62216 (14)	0.0465 (5)
H2	0.1288	0.3458	0.6221	0.056*
C3	0.17455 (7)	0.5475 (4)	0.58611 (14)	0.0472 (5)
H3	0.1592	0.6764	0.5615	0.057*
C4	0.21568 (7)	0.5486 (4)	0.58731 (14)	0.0439 (4)
H4	0.2287	0.6793	0.5646	0.053*
C5	0.23703 (6)	0.3505 (3)	0.62305 (12)	0.0360 (4)
C6	0.28059 (6)	0.3308 (3)	0.62037 (12)	0.0356 (4)
N2	0.30220 (5)	0.4922 (3)	0.58383 (13)	0.0462 (4)
C7	0.34788 (6)	0.2110 (3)	0.62361 (12)	0.0355 (4)
C8	0.38781 (6)	0.1017 (3)	0.62886 (12)	0.0352 (4)
C9	0.40005 (6)	−0.1039 (4)	0.67636 (13)	0.0404 (4)
H9	0.3820	−0.1905	0.7069	0.048*
C10	0.43937 (6)	−0.1812 (4)	0.67844 (15)	0.0466 (5)
H10	0.4479	−0.3192	0.7110	0.056*
C11	0.46602 (6)	−0.0542 (4)	0.63233 (15)	0.0506 (5)
H11	0.4926	−0.1041	0.6340	0.061*
C12	0.45270 (6)	0.1464 (4)	0.58412 (15)	0.0490 (5)
H12	0.4701	0.2327	0.5518	0.059*
N1	0.22023 (5)	0.1595 (3)	0.65940 (12)	0.0407 (4)
N3	0.34134 (5)	0.4227 (3)	0.58616 (12)	0.0451 (4)
N4	0.41472 (5)	0.2185 (3)	0.58340 (11)	0.0409 (4)
H4A	0.4070	0.3452	0.5526	0.049*
O1	0.41023 (6)	0.6149 (4)	0.46276 (12)	0.0709 (5)
O2	0.44211 (5)	0.9097 (3)	0.38647 (13)	0.0636 (5)
O3	0.46696 (6)	0.5156 (4)	0.39250 (18)	0.0877 (7)
O4	0.40605 (5)	0.6036 (3)	0.30479 (11)	0.0633 (5)
S1	0.30657 (2)	0.07805 (9)	0.66034 (3)	0.03868 (13)
Cl1	0.43216 (2)	0.66014 (8)	0.38557 (3)	0.03972 (13)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0471 (11)	0.0442 (11)	0.0460 (11)	−0.0084 (9)	0.0084 (9)	−0.0049 (9)
C2	0.0417 (10)	0.0575 (13)	0.0394 (10)	−0.0001 (9)	0.0012 (8)	−0.0126 (9)
C3	0.0527 (12)	0.0468 (12)	0.0404 (10)	0.0111 (10)	−0.0015 (9)	−0.0039 (9)
C4	0.0538 (12)	0.0384 (10)	0.0396 (10)	0.0011 (9)	0.0063 (9)	0.0025 (8)

C5	0.0436 (10)	0.0338 (9)	0.0304 (8)	−0.0010 (7)	0.0034 (7)	−0.0025 (7)
C6	0.0446 (10)	0.0312 (8)	0.0310 (8)	−0.0020 (7)	0.0044 (7)	0.0000 (7)
N2	0.0510 (10)	0.0359 (8)	0.0534 (10)	0.0008 (7)	0.0132 (8)	0.0067 (8)
C7	0.0413 (9)	0.0356 (9)	0.0300 (8)	−0.0057 (7)	0.0063 (7)	−0.0015 (7)
C8	0.0388 (9)	0.0390 (9)	0.0277 (8)	−0.0070 (8)	0.0041 (7)	−0.0033 (7)
C9	0.0453 (10)	0.0409 (10)	0.0363 (9)	−0.0046 (8)	0.0102 (8)	0.0025 (8)
C10	0.0467 (11)	0.0483 (11)	0.0443 (11)	0.0022 (9)	0.0034 (9)	0.0049 (9)
C11	0.0377 (10)	0.0630 (14)	0.0506 (12)	−0.0026 (10)	0.0036 (9)	−0.0001 (10)
C12	0.0400 (10)	0.0590 (13)	0.0487 (11)	−0.0120 (9)	0.0088 (9)	0.0047 (10)
N1	0.0440 (9)	0.0354 (8)	0.0432 (9)	−0.0012 (7)	0.0068 (7)	0.0003 (7)
N3	0.0494 (10)	0.0372 (8)	0.0504 (10)	−0.0038 (7)	0.0136 (8)	0.0049 (7)
N4	0.0420 (9)	0.0442 (9)	0.0368 (8)	−0.0073 (7)	0.0059 (7)	0.0052 (7)
O1	0.0841 (13)	0.0781 (12)	0.0533 (10)	−0.0105 (10)	0.0194 (9)	0.0201 (9)
O2	0.0704 (11)	0.0440 (9)	0.0776 (12)	−0.0167 (8)	0.0134 (9)	0.0017 (8)
O3	0.0481 (10)	0.0771 (13)	0.135 (2)	0.0194 (10)	−0.0025 (11)	−0.0011 (13)
O4	0.0663 (11)	0.0715 (11)	0.0486 (9)	−0.0082 (9)	−0.0074 (8)	−0.0029 (8)
S1	0.0399 (3)	0.0360 (2)	0.0406 (3)	−0.00179 (19)	0.00645 (19)	0.00837 (19)
Cl1	0.0366 (2)	0.0386 (2)	0.0434 (3)	−0.00349 (18)	0.00246 (18)	0.00549 (18)

Geometric parameters (Å, º)

C1—N1	1.332 (3)	C7—S1	1.7135 (18)
C1—C2	1.380 (3)	C8—N4	1.352 (2)
C1—H1	0.9300	C8—C9	1.375 (3)
C2—C3	1.380 (3)	C9—C10	1.384 (3)
C2—H2	0.9300	C9—H9	0.9300
C3—C4	1.377 (3)	C10—C11	1.379 (3)
C3—H3	0.9300	C10—H10	0.9300
C4—C5	1.382 (3)	C11—C12	1.366 (3)
C4—H4	0.9300	C11—H11	0.9300
C5—N1	1.341 (2)	C12—N4	1.334 (3)
C5—C6	1.470 (3)	C12—H12	0.9300
C6—N2	1.308 (2)	N4—H4A	0.8600
C6—S1	1.7178 (19)	O1—Cl1	1.4478 (17)
N2—N3	1.365 (2)	O2—Cl1	1.4244 (17)
C7—N3	1.306 (3)	O3—Cl1	1.4099 (19)
C7—C8	1.464 (3)	O4—Cl1	1.4250 (17)
N1—C1—C2	123.6 (2)	C8—C9—C10	119.62 (18)
N1—C1—H1	118.2	C8—C9—H9	120.2
C2—C1—H1	118.2	C10—C9—H9	120.2
C1—C2—C3	118.8 (2)	C11—C10—C9	120.2 (2)
C1—C2—H2	120.6	C11—C10—H10	119.9
C3—C2—H2	120.6	C9—C10—H10	119.9
C4—C3—C2	118.8 (2)	C12—C11—C10	118.8 (2)
C4—C3—H3	120.6	C12—C11—H11	120.6
C2—C3—H3	120.6	C10—C11—H11	120.6
C3—C4—C5	118.3 (2)	N4—C12—C11	120.09 (19)

C3—C4—H4	120.9	N4—C12—H12	120.0
C5—C4—H4	120.9	C11—C12—H12	120.0
N1—C5—C4	123.89 (19)	C1—N1—C5	116.58 (18)
N1—C5—C6	114.72 (17)	C7—N3—N2	112.18 (16)
C4—C5—C6	121.35 (18)	C12—N4—C8	123.04 (18)
N2—C6—C5	124.15 (18)	C12—N4—H4A	118.5
N2—C6—S1	114.66 (15)	C8—N4—H4A	118.5
C5—C6—S1	121.08 (14)	C7—S1—C6	86.35 (9)
C6—N2—N3	112.00 (17)	O3—Cl1—O2	111.20 (13)
N3—C7—C8	120.12 (17)	O3—Cl1—O4	110.83 (13)
N3—C7—S1	114.81 (15)	O2—Cl1—O4	109.99 (11)
C8—C7—S1	125.04 (14)	O3—Cl1—O1	109.78 (14)
N4—C8—C9	118.27 (18)	O2—Cl1—O1	107.57 (12)
N4—C8—C7	115.83 (17)	O4—Cl1—O1	107.34 (11)
C9—C8—C7	125.90 (17)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4*A*···O1	0.86	2.01	2.820 (2)	157
C11—H11···O2^{i}	0.93	2.49	3.228 (3)	136
C12—H12···O3^{i}	0.93	2.58	3.268 (3)	131

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.