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4-Chloroselanyl-3,5-diethyl-1*H*-pyrazol-2-ium chloride

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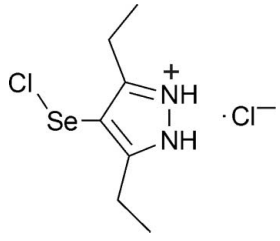
Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.004 Å; R factor = 0.026; wR factor = 0.049; data-to-parameter ratio = 20.4.

In the cation of the title compound, $C_7H_{12}ClN_2Se^+\cdot Cl^-$, the ethylene groups and the Se–Cl fragment adopt a *cis* configuration with a C—Se—Cl angle of 96.09 (6)°. In the crystal, intermolecular N—H···Cl hydrogen bonds link two cations and two chlorine anions into centrosymmetric clusters. π–π interactions between the pyrazole rings [centroid–centroid distance of 3.530 (2) Å] link these clusters into columns along [001] with short intermolecular Se···Cl^- contacts of 2.995 (1) Å.

Related literature

For reviews of organoselenium chemistry, see: Krief (1995); Freudendahl *et al.* (2009). For structural studies of bis(1*H*-pyrazol-4-yl)selenides, see: Seredyuk, Fritsky *et al.* (2010). For structural studies of *d*-metal complexes of bis(1*H*-pyrazol-4-yl)selenides, see: Seredyuk *et al.* (2007, 2009); Seredyuk, Moroz *et al.* (2010).



Experimental

Crystal data

$C_7H_{12}ClN_2Se^+\cdot Cl^-$
M_r = 274.05
Monoclinic, $P2_1/c$
a = 8.1944 (6) Å
b = 19.3719 (10) Å
c = 7.1241 (3) Å
β = 111.025 (6)°
V = 1055.60 (10) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 4.01 mm^{-1}
T = 120 K
0.30 × 0.21 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*XPREP* in *SHELXTL*; Sheldrick, 2008)
T_{min} = 0.379, T_{max} = 0.699
13385 measured reflections
2423 independent reflections
2040 reflections with $I > 2\sigma(I)$
R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.049
S = 1.04
2423 reflections
119 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.50 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···Cl1	0.82 (3)	2.22 (3)	3.0333 (19)	172 (3)
N2—H2···Cl1^{i}	0.81 (3)	2.22 (3)	3.030 (2)	178 (2)

Symmetry code: (i) $-x, -y, -z+3$.

Data collection: *COLLECT* (Bruker–Nonius, 2004); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2003); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV5179).

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supporting information

Acta Cryst. (2011). E**67**, o3083 [doi:10.1107/S1600536811043790]

4-Chloroselanyl-3,5-diethyl-1*H*-pyrazol-2-ium chloride

Maksym Seredyuk, Kateryna O. Znovjyak, Tetyana Yu. Sliva, Matti Haukka and Igor O. Fritsky

S1. Comment

Aryl selenides are central reagents in organoselenium chemistry (Krief, 1995; Freudendahl *et al.*, 2009). Pyrazole-based selenides are promising multidentate ligands for supramolecular frameworks and complexes of 3*d*-metals (Seredyuk *et al.*, 2007; Seredyuk *et al.*, 2009; Seredyuk, Moroz *et al.*, 2010). As a part of our study of the bis(1*H*-pyrazol-4-yl)selenides (Seredyuk, Fritsky *et al.*, 2010), we report the crystal structure of the title compound (Fig. 1).

In the title compound, between pairs of molecules of the compound strong N—H···Cl hydrogen bonds are observed with the distance N···Cl being 3.030 (2) and 3.0333 (19) Å (Table 1). The crystal packing exhibits $\pi\cdots\pi$ interactions between the pyrazol rings (centroid-centroid distance is 3.530 (2) Å) and short intermolecular Se···Cl^- contacts of 2.995 (1) Å.

S2. Experimental

Mixture of 3,5-diethyl-1*H*-pyrazole (1.241 g, 10 mmol), selenium dioxide (1.670 g, 15 mmol) and pyridine (25 ml) was refluxed 6 h, after that pyridine was distilled off under reduced pressure. Syrup-like residue was dissolved in 20 ml of conc. HCl and put in a fridge at 4°C for one week. The obtained precipitate was filtered off and dried. In the obtained mixture, well formed orange crystals are the target compound, whereas yellowish crystals are hydrochloride of bis(3,5-diethyl-1*H*-pyrazol-4-yl)selenide. $C_7H_{12}Cl_2N_2Se$ requires: C, 30.68; H, 4.41; N, 10.22. Found: C, 30.44; H, 4.54; N, 10.20.

S3. Refinement

N-bound H atoms were located on a difference Fourier map and refined isotropically. Other H atoms were placed in idealized position and constrained to ride on their parent atoms with the distances 0.98–0.99 Å and with U_{iso} = 1.2–1.5$_{eq}$ (parent atom).

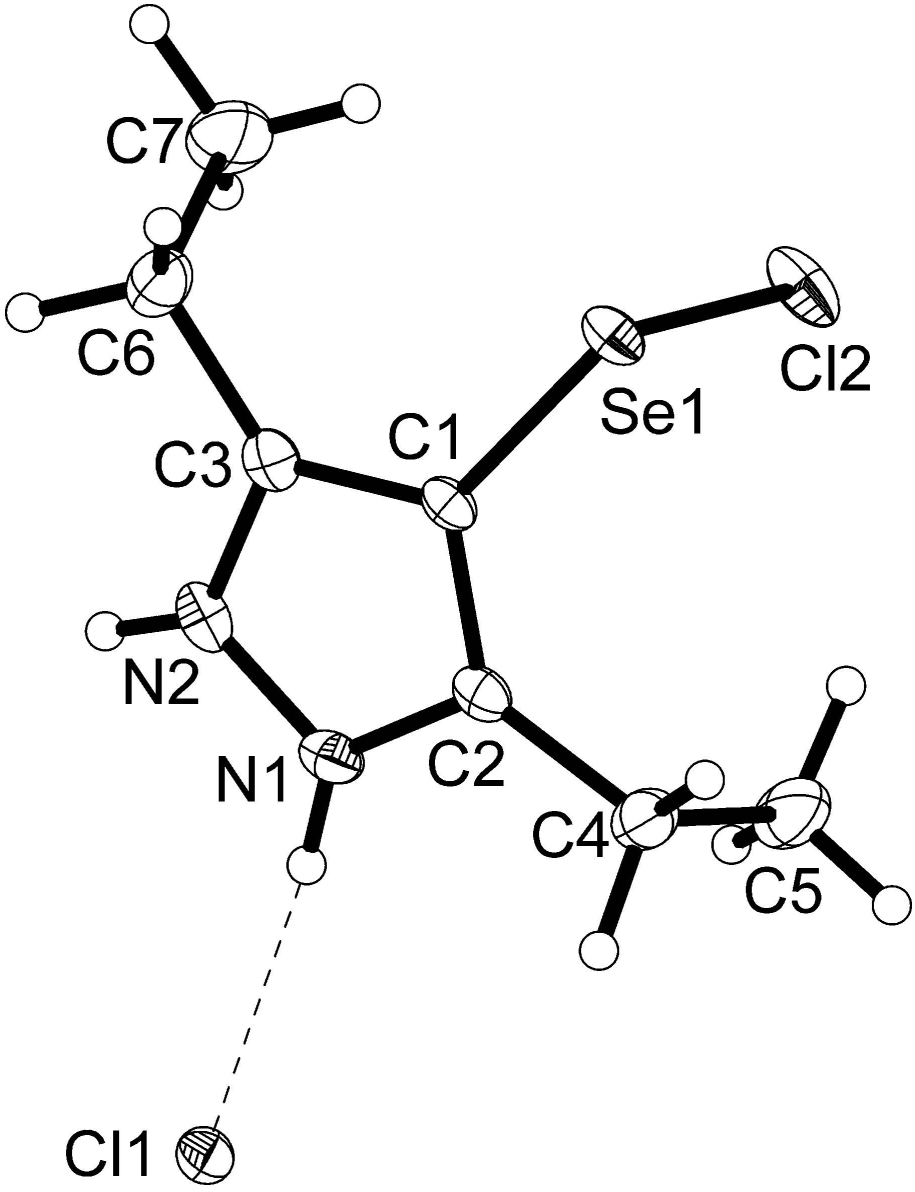

Figure 1

The content of asymmetric part of the title compound showing the atomic numbering and 50% probability displacement ellipsoids. Dashed line denotes hydrogen bond.

4-Chloroselanyl-3,5-diethyl-1*H*-pyrazol-2-ium chloride

Crystal data

$C_7H_{12}ClN_2Se^+\cdot Cl^-$
M_r = 274.05
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 8.1944 (6) Å
b = 19.3719 (10) Å
c = 7.1241 (3) Å
β = 111.025 (6)°
V = 1055.60 (10) Å^3
Z = 4
F(000) = 544
D_x = 1.724 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3966 reflections
θ = 1.0–27.5°
μ = 4.01 mm^{-1}

T = 120 K
Block, orange

0.30 × 0.21 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Horizontally mounted graphite crystal monochromator
Detector resolution: 9 pixels mm^{-1}
φ scans and ω scans with κ offset
Absorption correction: multi-scan (*XPREP* in *SHELXTL*; Sheldrick, 2008)

T_{min} = 0.379, T_{max} = 0.699
13385 measured reflections
2423 independent reflections
2040 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 27.5°, θ_{min} = 2.7°
h = −10→10
k = −23→25
l = −9→9

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.049
S = 1.04
2423 reflections
119 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 atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0163P)^2 + 1.0004P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.50 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 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}
Se1	0.09775 (3)	0.154947 (11)	0.72449 (3)	0.01773 (7)
Cl1	−0.26973 (7)	−0.02283 (3)	1.32107 (8)	0.01820 (12)
Cl2	0.00330 (8)	0.25802 (3)	0.77369 (9)	0.02668 (14)
N1	−0.0543 (3)	0.06371 (10)	1.1409 (3)	0.0188 (4)
H1	−0.119 (4)	0.0437 (15)	1.188 (4)	0.040 (8)*
N2	0.1181 (3)	0.06797 (9)	1.2431 (3)	0.0192 (4)
H2	0.162 (3)	0.0557 (13)	1.359 (4)	0.023 (7)*
C1	0.0658 (3)	0.11191 (10)	0.9452 (3)	0.0144 (4)
C2	−0.0913 (3)	0.08920 (10)	0.9570 (3)	0.0158 (4)
C3	0.1960 (3)	0.09761 (10)	1.1294 (3)	0.0164 (4)
C4	−0.2731 (3)	0.09086 (12)	0.8111 (4)	0.0235 (5)
H4A	−0.3384	0.0512	0.8368	0.028*
H4B	−0.2718	0.0860	0.6733	0.028*

C5	−0.3658 (3)	0.15699 (13)	0.8246 (5)	0.0352 (6)
H5A	−0.3615	0.1634	0.9627	0.053*
H5B	−0.4880	0.1545	0.7333	0.053*
H5C	−0.3082	0.1960	0.7864	0.053*
C6	0.3877 (3)	0.10861 (12)	1.2043 (4)	0.0247 (5)
H6A	0.4335	0.0933	1.1001	0.030*
H6B	0.4428	0.0796	1.3251	0.030*
C7	0.4393 (3)	0.18281 (13)	1.2570 (4)	0.0353 (6)
H7A	0.3884	0.2117	1.1371	0.053*
H7B	0.5670	0.1869	1.3064	0.053*
H7C	0.3960	0.1982	1.3617	0.053*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Se1	0.02534 (13)	0.01435 (11)	0.01690 (11)	−0.00085 (9)	0.01169 (9)	0.00111 (9)
Cl1	0.0180 (3)	0.0205 (3)	0.0173 (3)	0.0003 (2)	0.0077 (2)	0.0031 (2)
Cl2	0.0454 (4)	0.0144 (3)	0.0276 (3)	0.0047 (2)	0.0220 (3)	0.0042 (2)
N1	0.0212 (11)	0.0159 (9)	0.0228 (10)	−0.0016 (8)	0.0122 (9)	0.0014 (8)
N2	0.0281 (11)	0.0145 (9)	0.0156 (10)	0.0028 (8)	0.0084 (9)	0.0021 (8)
C1	0.0201 (11)	0.0097 (10)	0.0153 (10)	−0.0002 (8)	0.0086 (9)	−0.0004 (8)
C2	0.0209 (12)	0.0095 (9)	0.0194 (11)	0.0004 (8)	0.0101 (10)	−0.0010 (8)
C3	0.0218 (12)	0.0097 (10)	0.0178 (11)	0.0011 (8)	0.0072 (9)	−0.0030 (8)
C4	0.0181 (12)	0.0209 (12)	0.0307 (13)	−0.0004 (9)	0.0076 (10)	−0.0010 (10)
C5	0.0208 (12)	0.0229 (13)	0.0586 (18)	0.0025 (11)	0.0103 (12)	0.0011 (12)
C6	0.0196 (12)	0.0232 (12)	0.0276 (12)	0.0002 (10)	0.0039 (10)	−0.0023 (10)
C7	0.0311 (15)	0.0263 (13)	0.0429 (16)	−0.0088 (11)	0.0063 (13)	−0.0067 (12)

Geometric parameters (Å, º)

Se1—C1	1.8793 (19)	C4—H4A	0.9900
Se1—Cl2	2.2144 (6)	C4—H4B	0.9900
N1—C2	1.329 (3)	C5—H5A	0.9800
N1—N2	1.339 (3)	C5—H5B	0.9800
N1—H1	0.82 (3)	C5—H5C	0.9800
N2—C3	1.328 (3)	C6—C7	1.507 (3)
N2—H2	0.81 (3)	C6—H6A	0.9900
C1—C3	1.390 (3)	C6—H6B	0.9900
C1—C2	1.391 (3)	C7—H7A	0.9800
C2—C4	1.480 (3)	C7—H7B	0.9800
C3—C6	1.482 (3)	C7—H7C	0.9800
C4—C5	1.510 (3)		
C1—Se1—Cl2	96.09 (6)	C5—C4—H4B	109.2
C2—N1—N2	109.64 (18)	H4A—C4—H4B	107.9
C2—N1—H1	129 (2)	C4—C5—H5A	109.5
N2—N1—H1	121 (2)	C4—C5—H5B	109.5
C3—N2—N1	109.82 (19)	H5A—C5—H5B	109.5

C3—N2—H2	128.2 (18)	C4—C5—H5C	109.5
N1—N2—H2	121.9 (18)	H5A—C5—H5C	109.5
C3—C1—C2	107.06 (18)	H5B—C5—H5C	109.5
C3—C1—Se1	126.01 (16)	C3—C6—C7	113.1 (2)
C2—C1—Se1	126.93 (16)	C3—C6—H6A	109.0
N1—C2—C1	106.75 (19)	C7—C6—H6A	109.0
N1—C2—C4	121.10 (19)	C3—C6—H6B	109.0
C1—C2—C4	132.13 (19)	C7—C6—H6B	109.0
N2—C3—C1	106.72 (19)	H6A—C6—H6B	107.8
N2—C3—C6	121.5 (2)	C6—C7—H7A	109.5
C1—C3—C6	131.8 (2)	C6—C7—H7B	109.5
C2—C4—C5	112.1 (2)	H7A—C7—H7B	109.5
C2—C4—H4A	109.2	C6—C7—H7C	109.5
C5—C4—H4A	109.2	H7A—C7—H7C	109.5
C2—C4—H4B	109.2	H7B—C7—H7C	109.5

C2—N1—N2—C3	1.3 (2)	N1—N2—C3—C6	−179.63 (18)
Cl2—Se1—C1—C3	−101.57 (18)	C2—C1—C3—N2	0.0 (2)
Cl2—Se1—C1—C2	77.53 (18)	Se1—C1—C3—N2	179.22 (14)
N2—N1—C2—C1	−1.3 (2)	C2—C1—C3—C6	178.7 (2)
N2—N1—C2—C4	179.96 (18)	Se1—C1—C3—C6	−2.1 (3)
C3—C1—C2—N1	0.8 (2)	N1—C2—C4—C5	90.0 (3)
Se1—C1—C2—N1	−178.43 (15)	C1—C2—C4—C5	−88.4 (3)
C3—C1—C2—C4	179.4 (2)	N2—C3—C6—C7	−105.4 (3)
Se1—C1—C2—C4	0.1 (3)	C1—C3—C6—C7	76.0 (3)
N1—N2—C3—C1	−0.8 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Cl1	0.82 (3)	2.22 (3)	3.0333 (19)	172 (3)
N2—H2···Cl1^{i}	0.81 (3)	2.22 (3)	3.030 (2)	178 (2)

Symmetry code: (i) −*x*, −*y*, −*z*+3.