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(*Z*)-*N*-[2-(Dimethylammonio)ethyl]thioacetamide chloride

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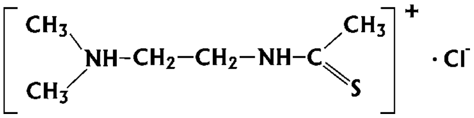
Key indicators: single-crystal X-ray study; T = 292 K; mean σ(C–C) = 0.002 Å; R factor = 0.030; wR factor = 0.089; data-to-parameter ratio = 18.4.

The thioamide and quaternary amine parts of the title compound, $C_6H_{15}N_2S^+\cdot Cl^-$, are mutually almost perpendicular, the dihedral angle being 80.6 (7)°. The thioamide group is planar and adopts a *Z* conformation, whereas the amine end of the cation is in an extended conformation. In the supramolecular structure, molecules are linked into centrosymmetric dimers by two hydrogen bonds: $N-H_{amine}\cdots Cl$ and $N-H_{thioamide}\cdots Cl$.

Related literature

For details of the synthesis, see Spychała (2000, 2003). For bond-length data, see: Allen (2002).



Experimental

Crystal data

$C_6H_{15}N_2S^+\cdot Cl^-$
M_r = 182.71
Triclinic, $P\overline{1}$
a = 5.9935 (2) Å
b = 7.7461 (3) Å
c = 10.8253 (4) Å
α = 79.489 (3)°
β = 79.796 (3)°
γ = 87.863 (3)°
V = 486.32 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.55 mm^{-1}
T = 292 (2) K
0.6 × 0.2 × 0.2 mm

Data collection

Kuma KM-4 CCD diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2007)
T_{min} = 0.785, T_{max} = 1.000 (expected range = 0.704–0.897)
4065 measured reflections
2332 independent reflections
1988 reflections with $I > 2\sigma(I)$
R_{int} = 0.008

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.089
S = 1.06
2332 reflections
127 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1···Cl1	0.883 (9)	2.174 (10)	3.0285 (11)	162.9 (16)
N4—H4···Cl1^i	0.863 (9)	2.325 (10)	3.1801 (12)	171.0 (16)

Symmetry code: (i) $-x+1, -y+1, -z+2$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens 1989) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2404).

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supplementary materials

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(*Z*)-*N*-[2-(Dimethylammonio)ethyl]thioacetamide chloride

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Comment

The structure of the title compound (I), is shown below. Dimensions are available in the archived CIF.

The asymmetric unit of the title compound, (I), consists of one $[C_6H_{15}N_2S]^+$cation and one chloride anion (Fig.1). The thioamide group is in *Z* configuration, its bond lengths are in agreement with the literature (Allen, 2002). The thioamide group is flat, the appropriate torsion angles adopt values close to 0° or 180° [S(5)—C(5)—N(4)—C(3) = τ_1 = −0.5 (2)°, C(51)—C(5)—N(4)—C(3) = τ_2 = −179.6 (1)°]. The quarternary amine end of the molecule is associated with conformational flexibility and it is apparent that the amine chain is in an almost extended conformation [C(12)—N(1)—C(2)—C(3) = τ_3 = 177.0 (1)°] and moreover, it lies in a plane that is nearly orthogonal to the thioamide plane, the dihedral angle between the least-squares planes is 80.6 (7)°. On the other hand, the amine and thioamide functions are mutually *gauche* oriented [N(1)—C(2)—C(3)—N(4) = τ_4 = 62.3 (2)°]. This conformation of the molecule causes some steric stress which is released by thioamide bond angles distortion from ideal values of 120°, *e.g.* the bond angles adopt values as follows: C(5)—N(4)—C(3) is 125.0 (1)°, S(5)—C(5)—N(4) 124.0 (1)°, C(3)—N(4)—H(4) 114.9 (1)°, C(51)—C(5)—N(4) 114.7 (1)°, although the sum of bond angles around C(5) and N(4) equals 360°. This diversity in bond angles seems to be the general property of amide and thioamide groups. The molecular conformation is stabilized by the intermolecular hydrogen bonds N—H···Cl which give rise to centrosymmetric dimers formation (Fig. 1). Each cation in the dimer participates in two hydrogen bonds to two chloride anions, N^+—*H*(amine)···Cl^- and *N*—*H*(thioamide)···Cl^-.

In supramolecular structure the dimers are ordered along the [010] direction one after the another thus forming alternate hydrophilic and hydrophobic segments. In the hydrophilic segments the chloride anions that interact with the cations *via* hydrogen bonds are located, whereas the hydrophobic segments are formed by two ribbons connected by van der Waals forces. Along the third direction, [100], the cations form stacks as the most efficient close packing motifs with the chloride anions forming columns in the channels of the close packing achieved by the cations.

Experimental

Starting from thioacetamide and the appropriate diaminoalkane, the title compound was obtained by the transamination Wallach reaction by refluxing the reaction mixture in ethanol. The reaction was carried out under literature conditions described in the previous papers (Spychała 2000, 2003). Solvent: 2-propanol / diethyl ether. Single crystals were grown from the hot solution by slow cooling.

Refinement

Hydrogen atoms were found from difference Fourier maps and refined except hydrogen atoms of three methyl groups, which were constrained to ride on their parent atom. The N—H distances were restrained to 0.88±0.01 Å.

Figures

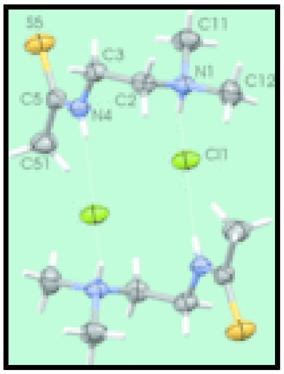

Fig. 1. Dimer of (I) generated by N^{+}—H(amine)···Cl^{-} and N—H(thioamide)···Cl^{-} hydrogen bonds (dashed lines). A view along the [100] direction, (Macrae *et al.*, 2006).

(*Z*)-*N*-[2-(Dimethylammonio)ethyl]thioacetamide chloride

Crystal data

$C_6H_{15}N_2S^{+}\cdot Cl^{-}$	$Z = 2$
$M_r = 182.71$	$F_{000} = 196$
Triclinic, $P\bar{1}$	$D_x = 1.248$ Mg m^{-3}
$a = 5.9935$ (2) Å	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$b = 7.7461$ (3) Å	Cell parameters from 2792 reflections
$c = 10.8253$ (4) Å	$\theta = 2.7$–29.6°
$\alpha = 79.489$ (3)°	$\mu = 0.55$ mm^{-1}
$\beta = 79.796$ (3)°	$T = 292$ (2) K
$\gamma = 87.863$ (3)°	Block, colourless
$V = 486.32$ (3) Å^3	0.6 × 0.2 × 0.2 mm

Data collection

Kuma KM-4 CCD diffractometer	2332 independent reflections
Radiation source: fine-focus sealed tube	1988 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.008$
Detector resolution: 8.1929 pixels mm^{-1}	$\theta_{max} = 29.7$°
$T = 292(2)$ K	$\theta_{min} = 3.0$°
ω–scan	$h = -8\rightarrow 6$
Absorption correction: multi-scan CrysAlis RED (Oxford Diffraction, 2007)	$k = -10\rightarrow 10$
$T_{min} = 0.785$, $T_{max} = 1.000$	$l = -14\rightarrow 11$
4065 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map

Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.030$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.089$	$w = 1/[\sigma^2(F_o^2) + (0.0493P)^2 + 0.0911P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
2332 reflections	$\Delta\rho_{max} = 0.36$ e Å^{-3}
127 parameters	$\Delta\rho_{min} = -0.27$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 $F^2 > 2\text{sigma}(F^2)$ 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}
Cl1	0.74439 (6)	0.68184 (5)	0.92798 (3)	0.04695 (12)
N1	0.43953 (18)	0.72292 (15)	0.72918 (10)	0.0369 (2)
C11	0.6186 (3)	0.7621 (2)	0.61349 (16)	0.0529 (4)
H11A	0.7143	0.6609	0.6068	0.073 (6)*
H11B	0.7081	0.8593	0.6201	0.077 (7)*
H11C	0.5489	0.7915	0.5390	0.070 (6)*
C12	0.3063 (3)	0.8834 (2)	0.75207 (18)	0.0564 (4)
H12A	0.4021	0.9661	0.7733	0.066 (6)*
H12C	0.1822	0.8526	0.8212	0.062 (5)*
H12B	0.2485	0.9351	0.6764	0.062 (5)*
C2	0.2817 (2)	0.5793 (2)	0.72500 (14)	0.0401 (3)
C3	0.3998 (2)	0.4127 (2)	0.69463 (14)	0.0417 (3)
N4	0.5321 (2)	0.33438 (15)	0.79089 (10)	0.0377 (2)
C5	0.7308 (2)	0.25637 (17)	0.76729 (13)	0.0368 (3)
C51	0.8327 (3)	0.1849 (2)	0.88345 (16)	0.0541 (4)
H51A	0.7944	0.0631	0.9114	0.134 (12)*
H51B	0.7743	0.2491	0.9503	0.148 (13)*
H51C	0.9945	0.1968	0.8630	0.127 (10)*
S5	0.86290 (6)	0.23364 (6)	0.62085 (4)	0.05189 (14)
H1	0.511 (3)	0.691 (2)	0.7946 (13)	0.052 (5)*
H2A	0.180 (3)	0.564 (2)	0.8055 (18)	0.052 (5)*

H2B	0.192 (3)	0.622 (2)	0.6625 (17)	0.046 (4)*
H3A	0.290 (3)	0.329 (2)	0.6874 (17)	0.055 (5)*
H3B	0.502 (3)	0.432 (2)	0.6142 (17)	0.043 (4)*
H4	0.468 (3)	0.338 (2)	0.8684 (10)	0.048 (4)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.03632 (18)	0.0692 (3)	0.03689 (19)	−0.00237 (15)	−0.00751 (13)	−0.01194 (16)
N1	0.0340 (5)	0.0447 (6)	0.0327 (5)	0.0040 (4)	−0.0078 (4)	−0.0072 (4)
C11	0.0460 (8)	0.0653 (10)	0.0444 (8)	−0.0118 (7)	0.0021 (6)	−0.0092 (7)
C12	0.0601 (10)	0.0474 (9)	0.0606 (10)	0.0114 (7)	−0.0097 (8)	−0.0103 (7)
C2	0.0302 (6)	0.0497 (8)	0.0408 (7)	0.0019 (5)	−0.0089 (5)	−0.0064 (6)
C3	0.0405 (7)	0.0499 (8)	0.0383 (7)	−0.0007 (6)	−0.0128 (6)	−0.0113 (6)
N4	0.0425 (6)	0.0418 (6)	0.0291 (5)	0.0026 (5)	−0.0063 (4)	−0.0079 (4)
C5	0.0394 (6)	0.0379 (7)	0.0347 (6)	−0.0031 (5)	−0.0083 (5)	−0.0080 (5)
C51	0.0602 (10)	0.0614 (11)	0.0432 (8)	0.0134 (8)	−0.0188 (7)	−0.0091 (7)
S5	0.0402 (2)	0.0778 (3)	0.0386 (2)	0.00595 (17)	−0.00335 (15)	−0.01740 (18)

Geometric parameters (Å, °)

N1—C12	1.488 (2)	C2—H2B	0.943 (18)
N1—C11	1.4908 (18)	C3—N4	1.4519 (18)
N1—C2	1.4988 (18)	C3—H3A	0.963 (19)
N1—H1	0.883 (9)	C3—H3B	0.962 (18)
C11—H11A	0.9600	N4—C5	1.3206 (18)
C11—H11B	0.9600	N4—H4	0.863 (9)
C11—H11C	0.9600	C5—C51	1.501 (2)
C12—H12A	0.9600	C5—S5	1.6786 (14)
C12—H12C	0.9600	C51—H51A	0.9600
C12—H12B	0.9600	C51—H51B	0.9600
C2—C3	1.510 (2)	C51—H51C	0.9600
C2—H2A	0.960 (19)		

C12—N1—C11	111.02 (13)	N1—C2—H2B	107.7 (10)
C12—N1—C2	109.51 (11)	C3—C2—H2B	109.2 (10)
C11—N1—C2	113.73 (11)	H2A—C2—H2B	106.1 (15)
C12—N1—H1	106.7 (12)	N4—C3—C2	112.06 (12)
C11—N1—H1	106.5 (12)	N4—C3—H3A	109.3 (11)
C2—N1—H1	109.1 (12)	C2—C3—H3A	109.9 (11)
N1—C11—H11A	109.5	N4—C3—H3B	106.9 (10)
N1—C11—H11B	109.5	C2—C3—H3B	112.5 (10)
H11A—C11—H11B	109.5	H3A—C3—H3B	105.9 (15)
N1—C11—H11C	109.5	C5—N4—C3	124.90 (12)
H11A—C11—H11C	109.5	C5—N4—H4	120.4 (12)
H11B—C11—H11C	109.5	C3—N4—H4	114.6 (12)
N1—C12—H12A	109.5	N4—C5—C51	114.66 (12)
N1—C12—H12C	109.5	N4—C5—S5	124.05 (10)
H12A—C12—H12C	109.5	C51—C5—S5	121.28 (11)

N1—C12—H12B	109.5	C5—C51—H51A	109.5
H12A—C12—H12B	109.5	C5—C51—H51B	109.5
H12C—C12—H12B	109.5	H51A—C51—H51B	109.5
N1—C2—C3	114.08 (11)	C5—C51—H51C	109.5
N1—C2—H2A	105.4 (11)	H51A—C51—H51C	109.5
C3—C2—H2A	113.9 (11)	H51B—C51—H51C	109.5

C12—N1—C2—C3	176.67 (13)	C3—N4—C5—C51	−179.64 (14)
C11—N1—C2—C3	51.81 (16)	C3—N4—C5—S5	−0.5 (2)
N1—C2—C3—N4	62.34 (16)	S5—C5—N4—H4	177.1 (14)
C2—C3—N4—C5	−142.40 (13)	C51—C5—N4—H4	−2.1 (14)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Cl1	0.883 (9)	2.174 (10)	3.0285 (11)	162.9 (16)
N4—H4···Cl1^{i}	0.863 (9)	2.325 (10)	3.1801 (12)	171.0 (16)

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+2.

Fig. 1