Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

1,1-Dimethylhydrazinium chloride

Alexei Merkoulov, Klaus Harms* and Jörg Sundermeyer

Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße, 35032 Marburg, Germany

Correspondence e-mail: harms@chemie.uni-marburg.de

Key indicators

Single-crystal X-ray study
T = 193 K
Mean σ(N–C) = 0.002 Å
R factor = 0.027
wR factor = 0.062
Data-to-parameter ratio = 12.7

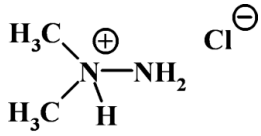
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 27 April 2005
Accepted 10 May 2005
Online 21 May 2005

The reaction of 1,1-dimethylhydrazine with a solution of HCl in Et_2O affords the anhydrous salt $Me_2N(H)NH_2^+\cdot Cl^-$. The crystal structure, determined by X-ray analysis, consists of two independent $[Me_2N(H)NH_2]^+$ cations and two Cl^- anions, which are connected *via* hydrogen bonds.

Comment

The title salt, (I), crystallizes in the space group $P2_1/n$ and the two independent ion pairs found in the asymmetric unit are presented in Fig. 1, with selected bond lengths and angles listed in Table 1. The bond lengths and angles in the $[Me_2N(H)NH_2]^+$ cation are similar to those found in the crystal structures with azide (Klapötke *et al.*, 1999) and nitrate (De Bonn *et al.*, 2001) anions.



(I)

The chloride anions form three hydrogen bonds with NH protons (Fig. 1), two with terminal NH_2 groups from two symmetry-related cations (N4—H5···Cl1/N4—H6···Cl1 and N2—H2···Cl2/N2—H3···Cl2) and one with the NH proton from the other independent cation (N1—H1···Cl1 and N3—H4···Cl2). Thus, each proton bonded to an N atom is involved in only one hydrogen bond with a Cl atom.

Furthermore, there are close contacts between the chloride anions and H atoms of methyl groups. Atom Cl1 has one such contact, while Cl2 exhibits four short contacts (see Table 2 and Fig. 1 for details).

The existence of C—H···Cl hydrogen bonds has been reviewed through a statistical analysis of data from the Cambridge Structural Database (Aakeröy *et al.*, 1999). It has been shown that chloride anions are better hydrogen-bond acceptors than neutral chlorine-containing molecules and the importance of such interactions to crystal engineering seems to have been vastly underestimated in the past. The parameters of the C—H···Cl contacts in (I) allow us to speculate that not only 'classical' N—H···Cl but also weak C—H···Cl hydrogen bonds are present.

Experimental

Me_2NNH_2 (10 ml, 131.5 mmol) was dissolved in dry Et_2O (20 ml). A 4.41 *M* solution of HCl (30 ml, 132.3 mmol) in Et_2O was added slowly

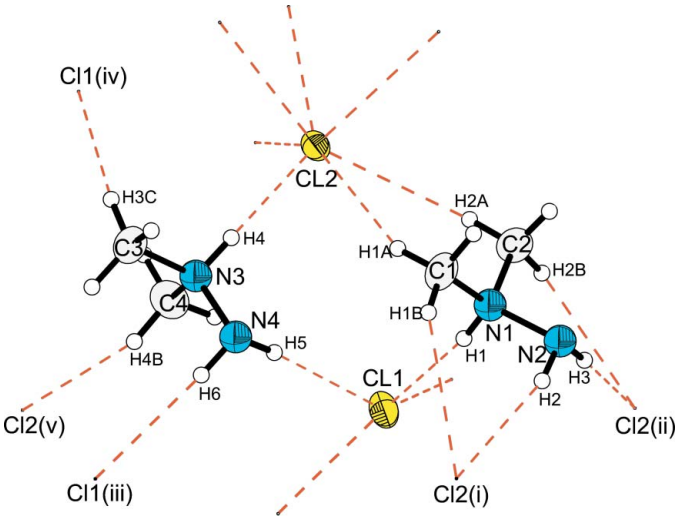


Figure 1
View of (I), showing the hydrogen bonds as dashed lines (50% probability displacement ellipsoids). Symmetry codes as in Table 2.

at 273 K. After warming to room temperature, the reaction was stirred for 1 h. The resulting white powder of (I) was filtered off and dried in vacuum (yield: 11.04 g, 87%). Cooling of a saturated CH_2Cl_2 solution at 243 K gave crystals suitable for X-ray analysis. ^{1}H NMR ($CDCl_3$, 500 MHz, 300 K): δ 7.36 (*s*, 3H, NH and NH_2), 3.01 (*s*, 6H, Me_2N). ^{13}C NMR ($CDCl_3$, 125 MHz, 300 K): δ 46.6 (Me_2N).

Crystal data

$C_2H_9N_2^+\cdot Cl^-$
M_r = 96.56
Monoclinic, $P2_1/n$
a = 9.7305 (9) Å
b = 10.5319 (10) Å
c = 10.4759 (10) Å
β = 90.475 (11)°
V = 1073.54 (18) Å^3
Z = 8
D_x = 1.195 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8000 reflections
θ = 2.8–26°
μ = 0.56 mm^{-1}
T = 193 (2) K
Needle, light orange
0.30 × 0.12 × 0.12 mm

Data collection

Stoe IPDS diffractometer
ω scans
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.853, T_{max} = 0.949
10 258 measured reflections
2077 independent reflections
1623 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
θ_{max} = 26°
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.062
S = 0.95
2077 reflections
163 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0392P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—N1	1.476 (2)	C4—N3	1.476 (2)
C2—N1	1.477 (2)	N1—N2	1.4546 (17)
C3—N3	1.482 (2)	N3—N4	1.4428 (18)
N2—N1—C1	109.16 (13)	N4—N3—C4	114.37 (14)
N2—N1—C2	108.89 (12)	N4—N3—C3	108.78 (13)
C1—N1—C2	112.43 (15)	C4—N3—C3	112.31 (13)
N2—N1—H1	110.4 (12)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···Cl1	0.83 (2)	2.27 (2)	3.0975 (15)	169.3 (16)
N2—H2···Cl2^{i}	0.91 (2)	2.47 (2)	3.3513 (16)	163.4 (16)
N2—H3···Cl2^{ii}	0.91 (2)	2.53 (2)	3.4342 (16)	171.6 (15)
N3—H4···Cl2	0.890 (19)	2.149 (19)	3.0369 (14)	175.9 (16)
N4—H5···Cl1	0.89 (2)	2.46 (2)	3.3382 (15)	172.5 (17)
N4—H6···Cl1^{iii}	0.87 (2)	2.52 (2)	3.3940 (16)	175.8 (18)
C1—H1*A*···Cl2	0.94 (2)	2.89 (2)	3.768 (2)	156.8 (16)
C1—H1*B*···Cl2^{i}	0.96 (2)	2.90 (2)	3.701 (2)	141.1 (14)
C2—H2*A*···Cl2	0.941 (19)	2.900 (18)	3.7817 (19)	156.4 (15)
C3—H3*C*···Cl1^{iv}	0.95 (2)	2.82 (2)	3.732 (2)	160.2 (16)
C2—H2*B*···Cl2^{ii}	0.97 (2)	2.88 (2)	3.721 (2)	146.4 (15)
C4—H4*B*···Cl2^{v}	0.93 (2)	2.87 (2)	3.5585 (19)	132.0 (17)

Symmetry codes: (i) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (iii) $2-x, -y, 1-z$; (iv) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (v) $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$.

All H atoms were located and refined isotropically; C—H distances are in the range 0.94 (2)–0.97 (2) Å and N—H distances are in the range 0.83 (2)–0.91 (2) Å.

Data collection: *EXPOSE* in *IPDS Software* (Stoe & Cie, 1999); cell refinement: *CELL* in *IPDS Software*; data reduction: *INTEGRATE* in *IPDS Software*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

References

Aakeröy, C. B., Evans, T. A., Seddon, K. R. & Palinko, I. (1999). *New J. Chem.* pp. 145–152.
Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
Brandenburg, K. (2001). *DIAMOND*. Version 2.1e. Crystal Impact GbR, Bonn, Germany.
De Bonn, O., Hammerl, A., Klapötke, T. M., Mayer, P., Piotrowski, H. & Zewen, H. (2001). *Z. Anorg. Allg. Chem.* **627**, 2011–5.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Klapötke, T. M., Nöth, H., Schwenk-Kirchera, H., Walther, W.-H. & Holl, G. (1999). *Polyhedron*, **18**, 717–9.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Stoe & Cie (1999). *IPDS Software*. Version 1.29. Stoe & Cie, Darmstadt, Germany.