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N,*N*-Dimethylguanidinium chloride

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Key indicators

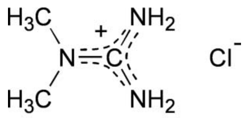
Single-crystal X-ray study
T = 100 K
Mean σ(N–C) = 0.002 Å
R factor = 0.035
wR factor = 0.084
Data-to-parameter ratio = 11.9

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

The title salt, $[(CH_3)_2NC(NH_2)_2]^+\cdot Cl^-$ or $C_3H_{10}N_3^+\cdot Cl^-$, is the first crystallographically characterized example of a dialkylguanidinium halide, $[R_2NC(NH_2)_2]^+\cdot X^-$. The essentially planar dimethylguanidinium cations are packed in a parallel alignment. Because of the delocalization of N electron lone pairs within the CN_3 unit, the core C$\overset{\cdots}{-}$N bonds [1.332 (3) Å] are significantly shorter than the terminal N—CH_3 bonds [1.461 (2) Å]. Chloride anions are fourfold coordinated by amine H atoms. Both ions are located on special positions, the dimethylguanidinium cation on the twofold axis along [010] and the Cl^- anion on the twofold axis along [001].

Comment

In our search for novel bis(silyl)carbodiimides as molecular precursors for non-oxide ceramics, we discovered by chance a straightforward procedure for synthesizing and crystallizing dialkylguanidinium chlorides. The original goal was to obtain amine-substituted disilylcarbodiimides of the general type $(R_2N)_3Si—N=C=N—Si(NR_2)_3$ by treatment of $(R_2N)_3SiCl$ with cyanamide, H_2NCN, by analogy with the synthesis of $R_3Si—N=C=N—SiR_3$ (R = alkyl) from R_3SiCl (Obermeyer *et al.*, 1994). However, besides the expected reaction, an N–N exchange also occurred. An Si-bonded amine group was replaced by cyanamide, thereby producing both dialkylamine R_2NH and polymeric species. The latter have so far not been characterized in more detail. Because of its low solubility in tetrahydrofuran, the title salt, (I), crystallized directly from the reaction solution. Although this compound was synthesized previously in 1922 from dicyandiamide and methylamine hydrochloride (Werner & Bell, 1922), no crystal structures of *N*,*N*-dialkylguanidinium halides have been published to date (Cambridge Structural Database, Version 5.28; Allen, 2002). The only crystal structure determined so far for guanidinium halide derivatives is that of guanidinium chloride, $C(NH_2)_3^+\cdot Cl^-$ (Theilacker, 1931; Haas *et al.*, 1965), which crystallizes in space group *Pbca* with Z = 8.



(I)

The most striking structural features of the guanidinium cation are its planarity [N$\overset{\cdots}{-}$C$\overset{\cdots}{-}$N angles of 119.3 (8), 119.7 (8) and 120.8 (8)°] and virtually equal C$\overset{\cdots}{-}$N bond lengths [1.318 (6), 1.325 (5) and 1.325 (6) Å].

In contrast with guanidinium chloride, compound (I) (Fig. 1) crystallizes in space group *Fddd* with Z = 16 (Fig. 2). The

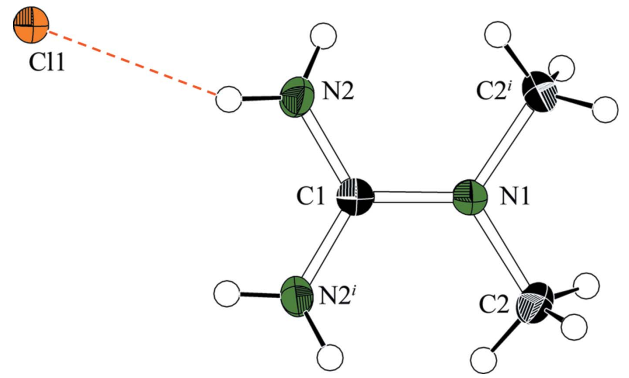


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. The dashed line represents the Cl$\cdots$H contact. [Symmetry code: (i) $-x + \frac{5}{4}, y, -z + \frac{1}{4}$.]

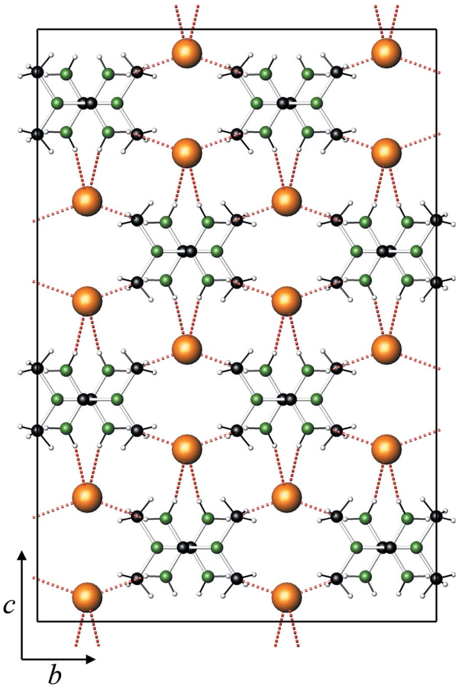


Figure 2
A packing diagram for (I), viewed along [100]. Dotted lines represent Cl$\cdots$H contacts, indicating that Cl^- anions have a distorted tetrahedral coordination environment.

dimethylguanidinium cations (located on Wyckoff sites 16*f*), which have C_2 symmetry, are packed in a parallel array. The C1$\overset{\cdots}{-}$N1 and C1$\overset{\cdots}{-}$N2 bond lengths (Table 1) are almost identical to those of the guanidinium cation. They are significantly shorter than the N1—C2 distance, reflecting the higher bond order of C1$\overset{\cdots}{-}$N1 and C1$\overset{\cdots}{-}$N2 due to the delocalization of N electron lone pairs in the CN_3 core. The sums of the angles around N1 and C1 are both 360°, indicating an essentially planar geometry, and the dihedral angle between the two planes is 10.9 (1)°.

The dotted lines in Fig. 2 depict H$\cdots$Cl contacts (Cl^- anions are located on Wyckoff sites 16*f*). Two H atoms of each guanidinium cation are involved in building the network. Each Cl^- anion interacts with four amine H atoms (from different symmetry-related cations), which are arranged in a distorted tetrahedral environment. H$\cdots$Cl separations are 2.46 (2) and 2.43 (3) Å for H1$\cdots$Cl1 and H2$\cdots$Cl1, respectively. There is no evidence for interaction of C-bonded H atoms with Cl^- anions (H$\cdots$Cl separations > 3.3 Å).

Experimental

All manipulations were performed in a purified Ar atmosphere using standard Schlenk techniques. Tetrahydrofuran (THF) was dried over Na–benzophenone and freshly distilled. Cyanamide (99% purity) was obtained from Sigma Aldrich and dried at 298 K and 10^{-3} mbar (1 bar = 100 000 Pa) for 5 h prior to use. $ClSi(NMe_2)_3$ was synthesized according to a procedure described in the literature from $SiCl_4$ and $HNMe_2$ in diethyl ether solution at 223 K (Rovai *et al.*, 1999). H_2NCN (8.0 g, 190 mmol) was dissolved in THF (100 ml) and the solution cooled to 203 K. A solution of $ClSi(NMe_2)_3$ (6.5 g, 33.3 mmol) in THF (500 ml) was added over a period of 3 h and the reaction mixture was subsequently allowed to warm to 298 K overnight. Crystallization of (I) and precipitation of a white amorphous solid occurred within 2 d. The colourless crystals formed predominantly near the surface of the solution and could be separated easily from the amorphous solid.

Crystal data

$C_3H_{10}N_3^+\cdot Cl^-$
M_r = 123.59
Orthorhombic, *Fddd*
a = 6.7568 (9) Å
b = 15.732 (2) Å
c = 23.364 (3) Å
V = 2483.5 (6) Å^3
Z = 16
Mo *Kα* radiation
μ = 0.50 mm^{-1}
T = 100 (2) K
0.40 × 0.05 × 0.05 mm

Data collection

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
T_{min} = 0.825, T_{max} = 0.975
4602 measured reflections
643 independent reflections
550 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.085
S = 1.17
643 reflections
54 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C1	1.332 (3)	N2—H2	0.85 (3)
N1—C2	1.461 (2)	C2—H3	0.92 (2)
C1—N2	1.332 (2)	C2—H4	0.94 (3)
N2—H1	0.81 (2)	C2—H5	0.94 (3)
C1—N1—C2	122.48 (11)	N2^i—C1—N2	119.2 (2)
C2—N1—C2^i	115.0 (2)	N2—C1—N1	120.41 (12)

Symmetry code: (i) $-x + \frac{5}{4}, y, -z + \frac{1}{4}$.

All H atoms were found in a difference map and refined isotropically with free coordinates.

o2768 Weinmann *et al.* • $C_3H_{10}N_3^+\cdot Cl^-$ *Acta Cryst.* (2007). E**63**, o2767–o2769

Data collection: *SMART32* (Bruker, 2000); cell refinement: *SAINT32* (Bruker, 2000); data reduction: *SAINT32*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 2005); software used to prepare material for publication: *SHELXL97*.

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Acta Cryst. (2007). E**63**, o2767–o2769 Weinmann *et al.* • $C_3H_{10}N_3^+\cdot Cl^-$ **o2769**