Kina Muller, Eric C. Hosten and Richard Betz*

The crystal structure of 1-chloro-2-(dimethylamino)ethane hydrochloride, $C_4H_{11}Cl_2N$

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Abstract

$C_4H_{11}Cl_2N$, monoclinic, $I2/a$ (no. 15), $a = 13.2374(12)$ Å, $b = 8.2108(6)$ Å, $c = 14.0114(14)$ Å, $\beta = 93.294(8)^\circ$, $V = 1520.4(2)$ Å³, $Z = 8$, $R_{gt}(F) = 0.0398$, $wR_{ref}(F^2) = 0.1174$, $T = 200$ K.

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The molecular structure is shown in the Figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The compound was obtained commercially (Fluka). Crystals suitable for the diffraction studies were taken directly from the provided product.

*Corresponding author: Richard Betz, Department of Chemistry, Nelson Mandela University, Summerstrand Campus (South), University Way, Summerstrand, PO Box 77000, Port Elizabeth, 6031, South Africa, E-mail: Richard.Betz@mandela.ac.za. <https://orcid.org/0000-0002-5730-2152>

Kina Muller and Eric C. Hosten, Department of Chemistry, Nelson Mandela University, Summerstrand Campus (South), University Way, Summerstrand, PO Box 77000, Port Elizabeth, 6031, South Africa. <https://orcid.org/0000-0003-4173-2550> (E.C. Hosten)

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.51 × 0.28 × 0.21 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.75 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	28.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	12,425, 1901, 0.018
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 1606
$N(param)_{refined}$:	89
Programs:	Bruker [1, 2], SHELX [3], WinGX/ORTEP [4], Mercury [5], PLATON [6]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U_{iso}^*/U_{eq}
Cl1	0.21545 (5)	0.22414 (9)	0.36596 (6)	0.0670 (2)
Cl2	−0.07570 (4)	0.25918 (6)	0.60437 (3)	0.04119 (17)
N1	−0.08466 (13)	0.2735 (2)	0.38777 (11)	0.0387 (4)
C4	−0.13420 (18)	0.1187 (3)	0.35806 (15)	0.0513 (5)
H4A	−0.094722	0.027046	0.385107	0.077*
H4B	−0.138063	0.111050	0.288144	0.077*
H4C	−0.202621	0.115459	0.381237	0.077*
C3	−0.14678 (18)	0.4140 (3)	0.35420 (17)	0.0563 (6)
H3A	−0.115731	0.514961	0.378940	0.084*
H3B	−0.214995	0.403503	0.377232	0.084*
H3C	−0.150823	0.416578	0.284159	0.084*
H1	−0.0803 (18)	0.274 (3)	0.4456 (19)	0.045 (6)*
C21 ^a	0.02001 (16)	0.2981 (3)	0.35545 (14)	0.0353 (5)
H21A ^a	0.040290	0.413162	0.365292	0.042*
H21B ^a	0.021096	0.273617	0.286324	0.042*
C11 ^a	0.09394 (17)	0.1886 (4)	0.41057 (17)	0.0448 (6)
H11A ^a	0.074303	0.073068	0.401402	0.054*
H11B ^a	0.094933	0.214080	0.479679	0.054*
C22 ^b	0.0212 (10)	0.197 (2)	0.3579 (9)	0.030 (4)
H22A ^b	0.026750	0.080790	0.376338	0.036*
H22B ^b	0.028635	0.206991	0.288247	0.036*
C12 ^b	0.0985 (10)	0.2983 (19)	0.4134 (11)	0.036 (4)
H12A ^b	0.097105	0.278220	0.482941	0.043*
H12B ^b	0.088493	0.415947	0.400542	0.043*

^aOccupancy: 0.876(5), ^bOccupancy: 0.124(5).

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.99 Å for methylene groups and C–H 1.00 Å for methine groups) and were included in the refinement in the riding model approximation, with $U(H)$ set to $1.2U_{eq}(C)$.

The H atoms of the methyl groups were allowed to rotate with a fixed angle around the C–C bond to best fit the experimental electron density (HFIX 137 in the *SHELX* program suite [3]), with $U(H)$ set to $1.5U_{eq}(C)$.

The nitrogen-bound H atom was located on a difference Fourier map and refined freely.

The central ethane bridge shows well-behaved orientational disorder over two positions. The two orientations are present in a ratio of 0.876(5) : 0.124(5).

Comment

The effect of size and steric pretense of large ions on chemical and spectroscopic properties of compounds have been a focus of research for many decades. Among the many effects that can be attributed to the spatial requirements of counterions have been the glass transition temperature in ionomers [7], surfactant modifying properties [8], the charge transfer in radical ions [9] and polymer-modified electrodes [10], as well as the structural and vibrational spectroscopic behaviour of DNA building blocks [11]. Furthermore, the benefit of choosing the adequate size of counterions to crystallize ionic compounds has been confirmed and reviewed on many occasions [12]. In continuation of our interest in metrical features of large cations [13–15] the structure of the title compound has been determined. The structure of a dinuclear chlorido-bridged molybdenum compound featuring the organic cation as counterion has been reported earlier [16].

The structure solution shows the presence of an ethane derivative bearing one chloro as well as one dimethylamino group as substituents on its two carbon atoms. The nitrogen atom is protonated to its ammonium state with a chloride anion countering the positive charge of the organic moiety. The ethane bridge shows well-behaved orientational disorder with the major component present in 87.6% of cases. C–N bond lengths cover a narrow range of only 1.477(3)–1.496(3) Å with the longest bond found towards the central ethyl chain. The C–Cl distance of 1.783(2) Å (found in the major disordered component) is in good agreement with other values found for this bond in compounds whose metrical parameters have been deposited with the Cambridge Structural Database [17].

In the crystal, classical hydrogen bonds of the N–H...Cl type are apparent next to C–H...Cl contacts whose range falls by more than 0.1 Å below the sum of van-der-Waals radii of the atoms participating in them. The donor atoms in the latter case are found in both hydrogen atoms of the methylene group bearing the dimethylamino group as well as one of the hydrogen atoms of the halogenated methylene group. For all contacts, only the chloride counterion serves as acceptor. In terms of graph-set analysis [18, 19], the descriptor for these contacts is *DDDD* at the unary level. In total, the entities of the asymmetric unit are connected to planes along [1 0 1].

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