

Diisopropylammonium chloride hemihydrate, a combined single-crystal and powder diffraction study

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Key indicators

Single-crystal and powder X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$

Disorder in solvent or counterion

R factor = 0.043

wR factor = 0.100

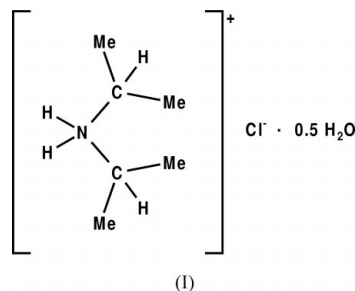
Data-to-parameter ratio = 15.2

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

By the reaction of diisopropylamine (dip) with hydrochloric acid and crystallization at room temperature, dipHCl, known from the literature, and the corresponding hemihydrate, $\text{C}_6\text{H}_{16}\text{N}^+\cdot\text{Cl}^- \cdot 0.5\text{H}_2\text{O}$ or dipHCl·0.5H₂O, have been obtained. By using a new humidity chamber for the powder diffraction study it has been proven that dipHCl reacts *via* a solid-solid phase transition to give dipHCl·0.5H₂O on increasing the relative humidity of the sample atmosphere. The cations and anions are connected by hydrogen bonds to form chains along the crystallographic [100] direction. The extended polymeric zigzag chains form layers in the *ac* plane, separated by water molecules. The cations and water molecules lie on crystallographic twofold rotation axes.

Comment

The crystal structures of all known diisopropylammonium halides (dipHHal; Hal = Cl, Br, I; Reiß, 2000) and that of dipH[HF₂] (Reiß, 2001, and references therein) have been found to be isostructural. All these structures are composed of hydrogen-bonded zigzag chains. Each dipH cation donates two hydrogen bonds to two neighbouring halide (pseudo-halide for the [HF₂] case) anions, while each anion acts as an acceptor for two hydrogen bonds. This motif may be classified, according to Etter's nomenclature (Etter *et al.*, 1990), as *C*(4). It is also known from the literature that diisopropylamine reacts with hydrochloric acid to form two modifications of dipHCl. A monoclinic (Adams *et al.*, 1997) and an orthorhombic structure (Prince *et al.*, 1990) have been reported and characterized by single-crystal methods. As dipH halides form both the monoclinic and the orthorhombic phase, it seemed to us worth investigating whether the inclusion of water into the structure was possible. Also, if the answer is yes, the second question should be: do the water molecules form hydrogen bonds with the chloride anion and the dip cations, or does additional water only fill the gaps in a different packing scheme?



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Dedicated to Professor A. Mewis on the occasion of his 60th birthday.

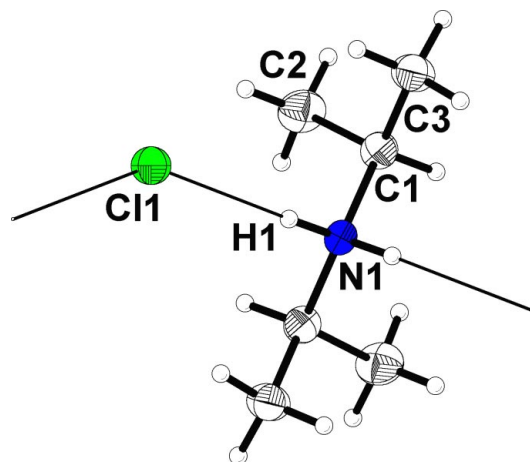


Figure 1
The diisopropylammonium cation and the neighbouring chloride anions, connected *via* hydrogen bonds to form chains along [100]. The displacement ellipsoids are drawn at the 50% probability level.

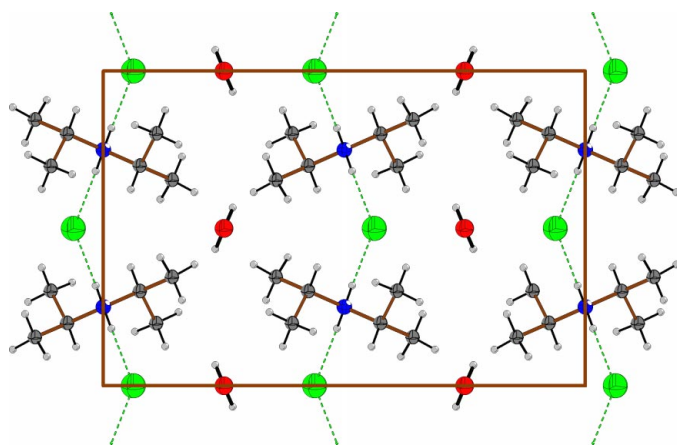


Figure 2
View of the hydrogen-bonded zigzag chains, separated by water molecules.

tals of the corresponding hemihydrate $\text{dipHCl} \cdot 0.5\text{H}_2\text{O}$. The dipH cation (Fig. 1) and the water molecules lie on twofold axes in the centrosymmetric orthorhombic space group $Ccca$ (No. 68). All C–C and N–C bond lengths in the dipH cation are in the expected range (Table 1). This structure is analogous to the anhydrous compounds, composed of hydrogen-bonded polymeric zigzag chains, with the dipH cations interconnected by chloride anions. The zigzag chains in the title compound are extended [N–Cl–N' $144.4(1)^\circ$ and Cl–N–Cl' $118.7(1)^\circ$], while the chains in the anhydrous compounds show a more kinked arrangement. The corresponding values derived for the monoclinic phase are N–Cl–N $97.0(1)$ and Cl–N–Cl' 113.3° ; for the orthorhombic modification they are N–Cl–N' $99.9(1)$ and Cl–N–Cl' $109.4(1)^\circ$. These chains are packed in the *ac* plane, with the stacks separated by water molecules (Fig. 2).

The question of whether a direct solid–solid phase transition occurs from the anhydrous phase to the corresponding hemihydrate and *vice versa* has been checked by using a humidity chamber for the powder diffraction study. A powder

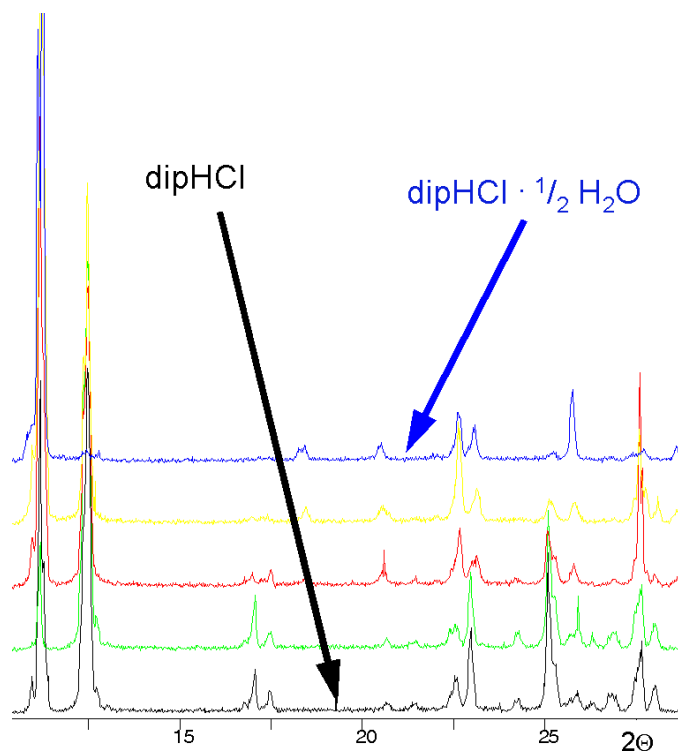


Figure 3
Powder diagrams showing the transition from dipHCl to $\text{dipHCl} \cdot 0.5\text{H}_2\text{O}$, taken at different humidity values of the sample atmosphere (40% black, 50% green, 60% red, 70% yellow and 75% blue).

sample containing only the orthorhombic modification of dipHCl was prepared from concentrated hydrochloric acid solution. Powder diffraction patterns at various relative humidities of the sample atmosphere, at room temperature, showed that the dipHCl transforms to $\text{dipHCl} \cdot 0.5\text{H}_2\text{O}$ (Fig. 3). A further increase of the relative humidity of the sample leads to a liquefaction of the sample.

The water molecules are found in cavities between the dipHCl stacks. According to difference Fourier syntheses and the results of refinement, only one of each pair of crystallographically equivalent sites for the water molecule within a cavity is occupied. The O···O distance of $2.791(16)$ Å for this hypothetical centrosymmetric water dimer makes it plausible that the fully occupied phase (monohydrate) also exists. On the other hand, an ordered refinement of these half-occupied water sites should cause a reduction of the space-group symmetry, with the disadvantage of serious correlations during the refinement process (*e.g.* Reiß & Engel, 2002). However, in this case we decided, according to the guidelines of space-group selection of structures that are potentially described in an unnecessarily low symmetry (Marsh *et al.*, 2002, and references therein), to choose the centrosymmetric space group $Ccca$.

Experimental

Diisopropylamine reacts readily with concentrated hydrochloric acid to give a colourless solution. From this solution were obtained brick-shaped crystals of dipHCl, together with some small thin platelets of

the dipHCl.0.5H₂O phase. The powder investigation was performed on a Philips PW1050 diffractometer (Cu K α radiation) equipped with a temperature humidity chamber (THC, Anton Paar, Graz). The sample was kept under a constant known relative humidity until equilibrium was reached, before a new measurement was initiated.

Crystal data

C₆H₁₆N⁺·Cl⁻·0.5H₂O
M_r = 146.66
 Orthorhombic, *Ccca*
a = 10.289 (2) Å
b = 15.723 (3) Å
c = 11.590 (2) Å
V = 1874.9 (6) Å³
Z = 8
D_x = 1.039 Mg m⁻³

Mo K α radiation
 Cell parameters from 5000 reflections
 θ = 2.6–25.7°
 μ = 0.34 mm⁻¹
T = 293 (2) K
 Platelet, colourless
 0.35 × 0.10 × 0.01 mm

Data collection

Stoe IPDS diffractometer
 φ scans
 Absorption correction: none
 11427 measured reflections
 819 independent reflections
 574 reflections with *I* > 2 σ (*I*)

*R*_{int} = 0.168
 θ_{max} = 25.0°
h = -12 → 12
k = -18 → 18
l = -13 → 13

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.043
wR(*F*²) = 0.100
S = 1.09
 819 reflections
 54 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.01P)^2 + 1.09P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.31 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0035 (10)

Table 1

Selected geometric parameters (Å, °).

N1—C1	1.513 (2)	C1—C3	1.516 (3)
C1—C2	1.510 (3)		
C1—N1—C1 ⁱ	117.7 (3)	C2—C1—C3	112.1 (2)
C2—C1—N1	110.93 (18)	N1—C1—C3	108.0 (2)
C1 ⁱ —N1—C1—C2	56.61 (17)	C1 ⁱ —N1—C1—C3	179.8 (2)

Symmetry code: (i) $\frac{1}{2} - x, -y, z$.

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H1···Cl1	0.899 (9)	2.302 (10)	3.1985 (14)	175 (2)

Methyl H atoms were refined riding on their corresponding C atom, allowed to rotate about the C—C bond, with a common *U*_{iso} value for each group. The atomic coordinates and an individual *U*_{iso} value for the H atom attached to the N atom were refined freely.

Data collection: *IPDS Software* (Stoe & Cie, 1998); cell refinement: *IPDS Software*; data reduction: *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001).

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