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Crystal structure of *N*,*N*,*N*-triethylhydroxylammonium chloride

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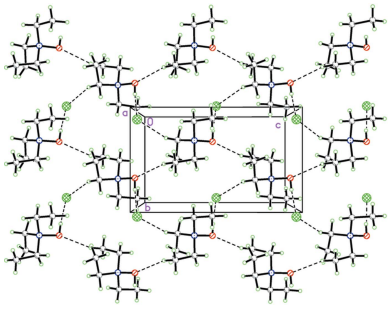
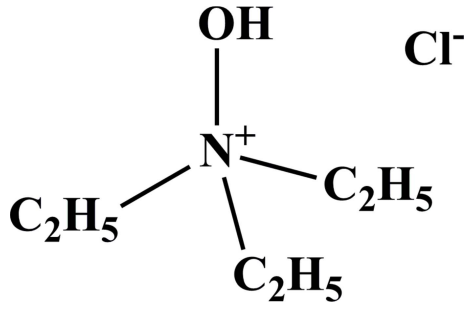
In the title molecular salt, $C_6H_{16}NO^+\cdot Cl^-$, two of the C—C—N—O groups in the cation adopt a *gauche* conformation [torsion angles = 62.86 (11) and −54.95 (13)°] and one an *anti* conformation [−177.82 (10)°. The cation and anion are linked by an O—H···Cl hydrogen bond. The extended structure displays C—H···Cl and C—H···O hydrogen bonds, resulting in layers lying parallel to the (100) plane: further C—H···Cl contacts connect the sheets into a three-dimensional network.

1. Chemical context

Triethylamine is often used to treat silica gel with the goal of reducing the acidity of the stationary phase during column chromatography purification. In a typical procedure, an eluant is mixed with triethylamine (1–3%), and this solvent mixture is used to prepare the silica gel slurry for manually packed columns. While the effect of the triethylamine on silica gel is known, no specific details could be found about the structural transformation of triethylamine itself. This work presents the result of the column chromatography purification of a dithiazolo[4,5-*a*:5′,4′-*c*]phenazine derivative using a dichloromethane:ethyl acetate mixture as eluant. Unexpectedly, the crystals obtained after slow solvent evaporation from an 'empty' fraction were identified as the title molecular salt, *N*,*N*,*N*-triethylhydroxylammonium chloride, **1**.





2. Structural commentary

The molecular structure of **1** is presented in Fig. 1. The C—N bond lengths [1.5090 (13)–1.5148 (13) Å] and the N—O bond length [1.4218 (11) Å] are in good agreement with mean reported geometries for 79 entries from the Cambridge Structural Database (CSD; Groom *et al.*, 2016) containing the

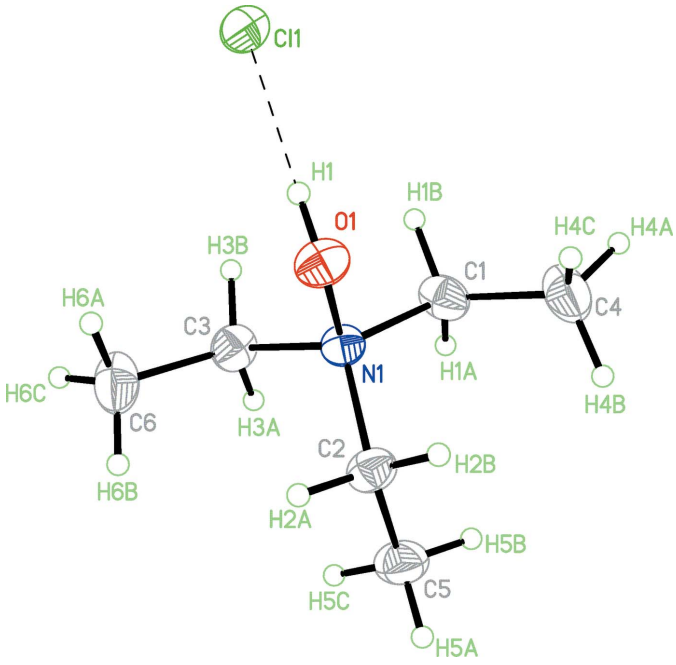


Figure 1
The molecular structure of **1**, with displacement ellipsoids drawn at the 50% probability level. The O1—H1···Cl1 hydrogen bond is shown as a dashed line (see Table 1).

C_3N—O—*R* (*R* = C, H) fragment: C—N 1.51 (3) Å and N—O 1.42 (2) Å and comparable to the analogous data in a closely related compound, *N*,*N*,*N*-trimethylhydroxylammonium chloride, **2** (1.488–1.489 Å for the N—C bonds and 1.429 Å for the N—O bond) (Jiang *et al.*, 2004; Rérat, 1960; Caron & Donohue, 1962). The hydroxyl hydrogen atom H1 participates in a strong hydrogen bond with the adjacent chloride anion (Table 1), which is also observed for **2**.

3. Supramolecular features

The O1—H1···Cl1 and C1—H1*A*···Cl1 hydrogen bonds assemble the constituent ions into spiral chains around 2_1 axes.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···Cl1	0.87 (2)	2.06 (2)	2.9330 (12)	175 (2)
C1—H1*A*···Cl1^{i}	0.934 (18)	2.888 (19)	3.7786 (15)	159.8 (15)
C2—H2*A*···Cl1^{ii}	0.955 (18)	2.943 (17)	3.6859 (16)	135.6 (14)
C3—H3*B*···Cl1	0.977 (19)	2.911 (19)	3.6203 (16)	130.3 (14)
C3—H3*A*···Cl1^{i}	0.93 (2)	2.93 (2)	3.7740 (19)	150.7 (14)
C4—H4*A*···Cl1^{iii}	1.02 (4)	2.98 (4)	3.9913 (18)	172 (2)
C5—H5*B*···O1^{iv}	0.97 (3)	2.50 (3)	3.4359 (18)	163 (2)

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

These chains are connected by C5—H5*B*···O1 hydrogen bonds into sheets lying parallel to the (100) plane (Fig. 2). There are four weak C—H···Cl contacts in the structure. The C2—H3*B*···Cl1 contact reinforces the O—H···Cl hydrogen bond; the C3—H3*A*···Cl1 hydrogen bond connects molecules within a sheet, while the C2—H2*A*···Cl1 and C4—H4*A*···Cl1 contacts connect the ions between the (100) sheets.

For comparison, the crystal packing of **2** is rather different. The cations in **2** lie on mirror planes and are arranged into chains along the [100] direction, being linked by O1–H1···Cl1 and C2–H5···Cl1 hydrogen bonds. The molecules in the chain are symmetrically related by a glide plane and C1—H2···Cl1 hydrogen bonds connect the chains into three-dimensional network. It is noteworthy that the oxygen atom does not participate as a proton acceptor in hydrogen bonding.

4. Database survey

A search of the Cambridge Structural Database (Groom *et al.*, 2016) revealed 221 crystal structures containing the C_3N–O fragment: 144 of them contain a C_3N^+—O^- fragment and 79 a C_3N–O–*R* fragment (*R* = C, H). While the additional connection of the oxygen atom increases the N—O bond length from 1.393 (18) to 1.42 (2) Å, the C—N bond lengths are not affected and remain at 1.51 (3) Å value. 31 structures in the CSD are salts of the C_3N^+–OH cation. In eight of them,

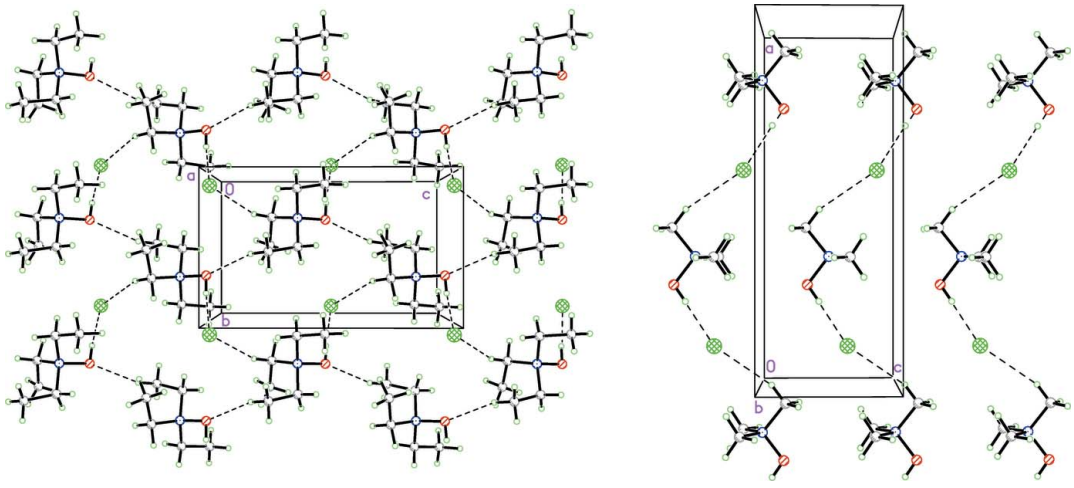


Figure 2
Layers in the crystal structures of (left) **1** and (right) **2**.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_6H_{16}NO^+\cdot Cl^-$
M_r	153.65
Crystal system, space group	Orthorhombic, $Pna2_1$
Temperature (K)	215
a, b, c (Å)	12.816 (5), 6.371 (3), 10.439 (4)
V (Å^3)	852.3 (6)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.38
Crystal size (mm)	0.40 × 0.20 × 0.05
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2008)
T_{min}, T_{max}	0.667, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12103, 2484, 2447
R_{int}	0.025
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.703
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.021, 0.056, 1.04
No. of reflections	2484
No. of parameters	146
No. of restraints	1
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.15, −0.14
Absolute structure	Flack x determined using 1146 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons et al., 2013)
Absolute structure parameter	0.046 (15)

Computer programs: *APEX2* and *SAINT* (Bruker, 2008), *SHELXS97* and *SHELXTL*(-(Sheldrick, 2008) and *SHELXL2014* (Sheldrick, 2015).

the anion is Cl^-, of which seven feature an O—H···Cl hydrogen bond (the O···Cl distance varies from 2.872 to 3.010 Å). The exception is the crystal structure of (1*S*,5*S*)-geneseroline hydrochloride monohydrate (refcode VAVZUN), in which the solvent water molecule accepts an O—H···O hydrogen bond from the C_3N^+–OH group.

5. Synthesis and crystallization

During the column chromatography purification of the dithiazolo[4,5-*a*:5′,4′-*c*]phenazine derivative using dichloromethane–ethyl acetate as eluant and Alfa–Aesar silica gel (stock # 42570; lot # K03T015; case # 632131-67-4) treated with triethylamine, a fraction containing a trace amount of the desired product was left over several days until compete evaporation of the solvents led to the formation of colourless plates of the title compound. Unexpectedly, the crystals were identified as *N*,*N*,*N*-triethylhydroxylammonium chloride; dichloromethane was probably the source of the chloride anion.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were all located in difference Fourier map and refined isotropically.

Acknowledgements

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supporting information

Acta Cryst. (2016). E**72**, 1607-1609 [https://doi.org/10.1107/S2056989016016169]

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Computing details

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT* (Bruker, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

N,*N*,*N*-Triethylhydroxylammonium chloride

Crystal data

$C_6H_{16}NO^+\cdot Cl^-$
M_r = 153.65
Orthorhombic, $Pna2_1$
a = 12.816 (5) Å
b = 6.371 (3) Å
c = 10.439 (4) Å
V = 852.3 (6) Å^3
Z = 4
$F(000)$ = 336
D_x = 1.197 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2230 reflections
θ = 3.6–32.3°
μ = 0.38 mm^{-1}
T = 215 K
Plate, colorless
0.40 × 0.20 × 0.05 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2008)
T_{min} = 0.667, T_{max} = 0.746
12103 measured reflections
2484 independent reflections
2447 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 30.0°, θ_{min} = 3.2°
h = −18→18
k = −8→8
l = −14→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.021
$wR(F^2)$ = 0.056
S = 1.04
2484 reflections
146 parameters
1 restraint
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0429P)^2 + 0.0129P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.034
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}
Absolute structure: Flack x determined using 1146 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons et al., 2013)
Absolute structure parameter: 0.046 (15)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.35543 (2)	−0.08505 (4)	0.50629 (5)	0.03438 (9)
O1	0.47318 (6)	0.30749 (12)	0.48070 (7)	0.02789 (17)
H1	0.4399 (16)	0.188 (4)	0.484 (3)	0.060 (6)*
N1	0.53046 (7)	0.29675 (12)	0.36425 (9)	0.02182 (16)
C1	0.45457 (9)	0.28944 (18)	0.25337 (10)	0.0299 (2)
H1B	0.4138 (19)	0.155 (4)	0.269 (2)	0.054 (5)*
H1A	0.4948 (15)	0.269 (3)	0.1798 (16)	0.031 (4)*
C2	0.59511 (9)	0.49467 (16)	0.36668 (10)	0.0269 (2)
H2B	0.5464 (16)	0.599 (3)	0.380 (2)	0.038 (5)*
H2A	0.6374 (13)	0.486 (3)	0.4418 (18)	0.028 (4)*
C3	0.59581 (10)	0.09863 (15)	0.36273 (11)	0.0278 (2)
H3B	0.5446 (14)	−0.015 (3)	0.358 (2)	0.038 (4)*
H3A	0.6338 (13)	0.106 (3)	0.287 (2)	0.030 (4)*
C4	0.38747 (11)	0.4836 (3)	0.24189 (13)	0.0404 (3)
H4C	0.3582 (16)	0.529 (4)	0.320 (2)	0.049 (6)*
H4B	0.4278 (16)	0.602 (3)	0.207 (2)	0.040 (5)*
H4A	0.328 (3)	0.450 (5)	0.181 (4)	0.086 (10)*
C5	0.66019 (11)	0.5267 (2)	0.24769 (13)	0.0347 (2)
H5C	0.712 (2)	0.420 (4)	0.240 (3)	0.077 (8)*
H5B	0.616 (2)	0.543 (4)	0.173 (3)	0.064 (7)*
H5A	0.6950 (19)	0.650 (4)	0.252 (2)	0.060 (6)*
C6	0.66688 (14)	0.0771 (2)	0.47737 (14)	0.0392 (3)
H6C	0.7011 (19)	−0.051 (4)	0.471 (2)	0.054 (6)*
H6B	0.7175 (18)	0.182 (4)	0.478 (3)	0.066 (7)*
H6A	0.6251 (18)	0.078 (3)	0.562 (3)	0.044 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.03250 (14)	0.03626 (14)	0.03439 (14)	−0.00604 (8)	−0.00249 (12)	0.00905 (11)
O1	0.0323 (4)	0.0302 (4)	0.0212 (4)	−0.0008 (3)	0.0078 (3)	−0.0021 (2)
N1	0.0231 (4)	0.0232 (3)	0.0192 (3)	−0.0007 (3)	0.0026 (3)	−0.0014 (3)
C1	0.0257 (4)	0.0417 (6)	0.0222 (4)	−0.0034 (4)	−0.0018 (4)	−0.0025 (4)
C2	0.0306 (5)	0.0230 (4)	0.0269 (5)	−0.0050 (3)	−0.0005 (4)	−0.0003 (4)
C3	0.0302 (5)	0.0236 (4)	0.0296 (5)	0.0037 (3)	0.0035 (4)	−0.0019 (4)
C4	0.0291 (6)	0.0589 (8)	0.0333 (6)	0.0091 (5)	−0.0011 (5)	0.0093 (6)
C5	0.0330 (6)	0.0403 (6)	0.0310 (6)	−0.0095 (5)	0.0017 (5)	0.0058 (5)
C6	0.0396 (6)	0.0409 (7)	0.0371 (8)	0.0117 (5)	−0.0027 (5)	0.0067 (5)

Geometric parameters (Å, º)

N1—O1	1.4218 (11)	C3—H3B	0.977 (19)
O1—H1	0.87 (2)	C3—H3A	0.93 (2)
N1—C2	1.5090 (13)	C4—H4C	0.94 (3)
N1—C1	1.5126 (14)	C4—H4B	0.987 (19)
N1—C3	1.5148 (13)	C4—H4A	1.02 (4)
C1—C4	1.5113 (19)	C5—H5C	0.96 (3)
C1—H1B	1.01 (2)	C5—H5B	0.97 (3)
C1—H1A	0.934 (18)	C5—H5A	0.91 (3)
C2—C5	1.5101 (18)	C6—H6C	0.93 (2)
C2—H2B	0.921 (19)	C6—H6B	0.93 (2)
C2—H2A	0.955 (18)	C6—H6A	1.03 (3)
C3—C6	1.5103 (19)		
N1—O1—H1	104.2 (17)	C6—C3—H3A	111.4 (11)
O1—N1—C2	103.23 (7)	N1—C3—H3A	104.8 (11)
O1—N1—C1	108.89 (8)	H3B—C3—H3A	110.2 (16)
C2—N1—C1	113.06 (8)	C1—C4—H4C	114.1 (16)
O1—N1—C3	109.55 (8)	C1—C4—H4B	111.0 (11)
C2—N1—C3	113.13 (8)	H4C—C4—H4B	107 (2)
C1—N1—C3	108.77 (8)	C1—C4—H4A	107.6 (18)
C4—C1—N1	113.66 (10)	H4C—C4—H4A	108 (3)
C4—C1—H1B	114.1 (13)	H4B—C4—H4A	109 (2)
N1—C1—H1B	103.7 (14)	C2—C5—H5C	111 (2)
C4—C1—H1A	111.2 (12)	C2—C5—H5B	110.9 (18)
N1—C1—H1A	106.2 (12)	H5C—C5—H5B	115 (3)
H1B—C1—H1A	107.3 (17)	C2—C5—H5A	110.5 (16)
N1—C2—C5	113.73 (9)	H5C—C5—H5A	106 (2)
N1—C2—H2B	103.4 (11)	H5B—C5—H5A	103 (2)
C5—C2—H2B	113.7 (12)	C3—C6—H6C	107.9 (16)
N1—C2—H2A	106.1 (12)	C3—C6—H6B	111.1 (16)
C5—C2—H2A	111.7 (10)	H6C—C6—H6B	108 (2)
H2B—C2—H2A	107.5 (17)	C3—C6—H6A	111.4 (14)
C6—C3—N1	113.62 (9)	H6C—C6—H6A	108.0 (19)
C6—C3—H3B	112.2 (12)	H6B—C6—H6A	111 (2)
N1—C3—H3B	104.2 (11)		
O1—N1—C1—C4	62.86 (11)	C3—N1—C2—C5	64.73 (12)
C2—N1—C1—C4	−51.26 (13)	O1—N1—C3—C6	−54.95 (13)
C3—N1—C1—C4	−177.82 (10)	C2—N1—C3—C6	59.62 (13)
O1—N1—C2—C5	−176.96 (9)	C1—N1—C3—C6	−173.87 (10)
C1—N1—C2—C5	−59.47 (12)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···Cl1	0.87 (2)	2.06 (2)	2.9330 (12)	175 (2)

C1—H1*A*···Cl1^{i}	0.934 (18)	2.888 (19)	3.7786 (15)	159.8 (15)
C2—H2*A*···Cl1^{ii}	0.955 (18)	2.943 (17)	3.6859 (16)	135.6 (14)
C3—H3*B*···Cl1	0.977 (19)	2.911 (19)	3.6203 (16)	130.3 (14)
C3—H3*A*···Cl1^{i}	0.93 (2)	2.93 (2)	3.7740 (19)	150.7 (14)
C4—H4*A*···Cl1^{iii}	1.02 (4)	2.98 (4)	3.9913 (18)	172 (2)
C5—H5*B*···O1^{iv}	0.97 (3)	2.50 (3)	3.4359 (18)	163 (2)

Symmetry codes: (i) −*x*+1, −*y*, *z*−1/2; (ii) *x*+1/2, −*y*+1/2, *z*; (iii) −*x*+1/2, *y*+1/2, *z*−1/2; (iv) −*x*+1, −*y*+1, *z*−1/2.