Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Redetermination of triethylammonium chloride in the space group $P31c$

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Received 2 June 2004
Accepted 11 June 2004
Online 10 July 2004

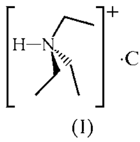
The structure of triethylammonium chloride, $C_6H_{16}N^+\cdot Cl^-$, has been redetermined in the space group $P31c$. In contrast with previous refinements in the space group $P6_3mc$, no disorder of the triethylammonium cation was observed.

Comment

The structure of triethylammonium chloride has been reported four times to date (Hendricks, 1928; Genet, 1965; James *et al.*, 1985; Ilyukhin, 2000). All four structure determinations were made in the space group $P6_3mc$ (No. 186) and showed 'propeller'-like disorder of the cation (Fig. 1) caused by a crystallographic mirror plane. Two closely related models were used in the later refinements. In the first, both independent C atoms occupy general positions [12 (*d*): x, y, z; Genet, 1965; James *et al.*, 1985; Fig. 1(*a*)]. In the second, the methylene C atom lies on a general position, while the methyl C atom lies on the mirror plane [6 (*c*): $x, \bar{x}, z$; Ilyukhin, 2000; Fig. 1(*b*)].

Such disorder is a common feature of the Et_3NH^+ cation. A total of 379 structures containing the triethylammonium cation are reported in the Cambridge Structural Database (CSD, Version 5.25; Allen, 2002). Of these, 126 structures are disordered (33.2%) and 76 structures (20.1%) possess the disordered cation. These figures are noticeably higher than the statistical appearance of disorder in the CSD (18.2%; Allen, 2002). The same type of disorder was observed previously for some other trialkylammonium derivatives with approximate C_{3v} symmetry, namely silatranes (Zaitseva *et al.*, 1996) and germatranes (Karlov *et al.*, 2001). These two structures were refined in the space group *Pnma*. However, refinements in the lower-symmetry space group $Pna2_1$ retain the 'propeller'-like disorder, with occupancy ratios $\simeq$ 0.5:0.5. On the contrary, the refinement of $[NHEt_3][Sn(acac)Cl_4]$ in the lower-symmetry group led to an ordered cation, but was not found to be convincing (Korte *et al.*, 1988). Against this background, we present here a further redetermination of the structure of triethylammonium chloride, (I) (Fig. 2).

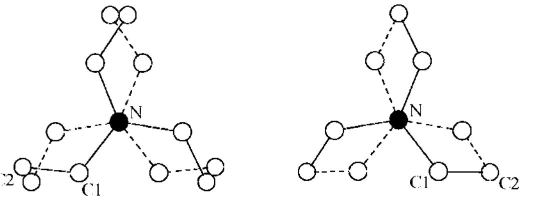
A new data set for (I) was collected on a Bruker SMART CCD diffractometer at 120 K. The systematic absences were consistent with the space groups $P31c$ (No. 159) and $P6_3mc$. Comparison of the $|F_o(hkl)|$ and $|F_o(hk\bar{l})|$ values points to $P6_3mc$, since their equality holds in $P6_3mc$ but not in $P31c$. However, the mean value of $|E^2 - 1|$ (0.678) was lower than expected for non-centrosymmetric crystals (Herbst-Irmer & Sheldrick, 1998).



(I)

At first, the structure was refined in the higher symmetry group $P6_3mc$. The model of Ilyukhin (2000) was found more appropriate and the final refinement converged to $R_1 = 0.054$ for 395 independent reflections with $I > 2\sigma(I)$ and 29 parameters. The highest difference peak was 0.55 e Å^{-3}. However, the Flack (1983) parameter was found to be poorly determined [0.00 (39)], and the use of the racemic TWIN instruction did not led to any improvement of results. Subsequently, the structure was solved and refined in the space group $P31c$. The disorder of the cation disappeared and the refinement led to a residual $R_1 = 0.072$ for 661 reflections with $I > 2\sigma(I)$ and 47 parameters. The highest difference peak was 0.82 e Å^{-3}.

The factor K = mean(F_o^2)/mean(F_c^2) for low-intensity reflections was slightly greater than 1 and did not directly indicate the presence of twinning (Herbst-Irmer & Sheldrick,



(*a*) (*b*)

Figure 1
The 'propeller'-like disorder of the Et_3NH^+ cation, viewed along the *c* axis, showing (*a*) the model of Genet (1965) and (*b*) the model of Ilyukhin (2000).

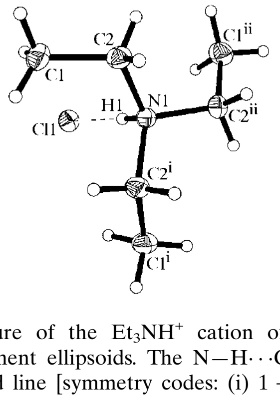


Figure 2
The ordered structure of the Et_3NH^+ cation of (I), showing 50% probability displacement ellipsoids. The N—H$\cdots$Cl hydrogen bond is denoted by a dashed line [symmetry codes: (i) $1 - y, 1 + x - y, z$; (ii) $y - x, 1 - x, z$].

DOI: 10.1107/S0108270104014209

1998). Later, the TWIN operator relative to the mirror plane ($\bar{1}00$, 110, 001) was included. This immediately resulted in the significant decrease of R_1 to 0.019 [48 parameters, Flack parameter 0.06 (6), highest difference peak 0.18 e Å^{-3}]. The volume fraction of twin components converged to 0.5. Kahlenberg (1999) noted that, in such cases, standard Yeates and Britton statistical tests for merohedral twinning fail. Thus, the choice of the space group may be made on the basis of the final residual parameters only.

Experimental

Crystals of (I) were grown from a solution in ethanol–water (1:1). Long needles (15 mm) were cut into small pieces of suitable size.

Crystal data

$C_6H_{16}N^+ \cdot Cl^-$
$M_r = 137.65$
Trigonal, *P*31*c*
$a = 8.2542$ (2) Å
$c = 6.9963$ (2) Å
$V = 412.81$ (2) Å^3
$Z = 2$
$D_x = 1.107$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 3089 reflections
$\theta = 2.8$–$30.0°$
$\mu = 0.38$ mm^{-1}
$T = 120$ (2) K
Block, colourless
0.40 × 0.10 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
3185 measured reflections
665 independent reflections
661 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.014$
$\theta_{\rm max} = 28.0°$
$h = -5 \rightarrow 10$
$k = -10 \rightarrow 9$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.047$
$S = 1.04$
665 reflections
48 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0415P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.18$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.09$ e Å^{-3}
Absolute structure: Flack (1983), with 297 Friedel pairs
Flack parameter = 0.06 (6)

The ammonium H atom was found from a difference Fourier synthesis. Other H atoms were placed in calculated positions. Both positional and displacement parameters for all H atoms were refined.

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.5053 (13)	C1—C2	1.5160 (18)
C2—N1—C2$^{\rm i}$	111.18 (11)	N1—C2—C1	112.23 (13)

Symmetry code: (i) $1 - y, 1 + x - y, z$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Bruker, 2000); software used to prepare material for publication: *SHELXTL-Plus*.

The authors thank Dr S. Z. Vatsadze for providing crystals of (I). AVC is grateful to the Royal Society of Chemistry for an RSC Journal Grant for International Authors.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1163). Services for accessing these data are described at the back of the journal.

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