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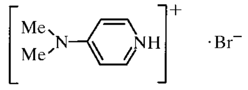
The crystal and molecular structure of 4-dimethylaminopyridinium bromide, $C_7H_{11}N_2^{+}\cdot Br^{-}$, (I), is built up by hydrogen-bonded dimers of crystallographic 222 symmetry and four short C—H...halogen contacts. It is remarkable that (I) and 4-dimethylaminopyridinium chloride are not isostructural.

Comment

It is a long tradition in our group to investigate the formation of Lewis-acid-base complexes of the silicon halides (Adley *et al.*, 1972; Bolte & Kettner (1998; Fleischer *et al.*, 1996; Klebe *et al.*, 1985; Spangenberg, 1999).

In the course of our research work several reactions of different silanes with tertiary organic nitrogen bases were performed. The afforded reaction products are very susceptible to moisture and, as a result of that, it sometimes happens that only crystals of the hydrolysed compounds are obtained (Hensen *et al.*, 1998; Bolte & Kettner, 1998).

The molecule of (I) with $C2_v$ symmetry has crystallographic *C*2 symmetry. The atoms Br1, H1, N1, C4 and N4 are located on a twofold rotation axis. The NH group forms a bifurcated hydrogen bond to two symmetry equivalent Br^- ions (H1···Br1 2.80 Å, N1—H1···Br1 132.7°) resulting in a dimer of crystallographic 222 symmetry. Furthermore, the crystal packing is stabilized by short Br···H contacts: H2···Br1 2.90 Å, C2—H2···Br1 124.7°, and H3···Br1^{i} 2.99 Å, C3—H3···Br1^{i} 134.2° [symmetry code: (i) $3/2 - x, \frac{1}{2}-y, -z$].



(I)

(I) crystallizes in planes parallel to (100). However, the molecules in a plane are not exactly coplanar, but twisted by 4.88 (3)° relative to each other.

The molecular geometry of the title compound is as expected. Bond lengths and angles adopt the usual values.

It is remarkable that the exchange of Br^- and Cl^- in 4-dimethylaminopyridinium complexes leads to different crystal structures: (I) and 4-dimethylaminopyridinium chloride (Bryant & King, 1992) are not isostructural. This lack of isostructurality has already been observed for other small pyridinium complexes (Faber *et al.*, 1999)

As previously published structures of 4-dimethylaminopyridinium suggest (Biradha *et al.*, 1995; Chao & Schempp, 1977), 4-dimethylaminopyridinium changes its packing arrangement rather easily as other small molecules are incorporated into the crystal.

Experimental

The title compound was obtained accidentally as part of solubility studies on silicon complexes resulting from the reaction of $SiBr_2Cl_2$ with 4-dimethylaminopyridine (DMAP). In chloroforme, DMAP reacts with $SiBr_2Cl_2$ to yield a white powder that is readily dissolved in methyl or ethyl alcohol. In hot propanol or hot butanol the substance dissolves equally well and yields needles of the title compound upon cooling.

Crystal data

$C_7H_{11}N_2^{+}\cdot Br^{-}$
$M_r = 203.09$
Orthorhombic, *Fddd*
$a = 6.9804$ (8) Å
$b = 19.256$ (2) Å
$c = 26.131$ (3) Å
$V = 3512.4$ (7) Å^3
$Z = 16$
$D_x = 1.536$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 502 reflections
$\theta = 1$–20°
$\mu = 4.613$ mm^{-1}
$T = 293$ (2) K
Plate, colourless
0.30 × 0.20 × 0.10 mm

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.338, T_{\max} = 0.656$
16371 measured reflections
782 independent reflections
506 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.081$
$\theta_{\max} = 25.02°$
$h = -8 \rightarrow 8$
$k = -22 \rightarrow 22$
$l = -30 \rightarrow 30$
75 standard reflections
frequency: 1200 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.100$
$S = 1.018$
782 reflections
49 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0552P)^2 + 4.7275P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.236$ e Å^{-3}
$\Delta\rho_{\min} = -0.253$ e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$Br1	0.86	2.80	3.446 (4)	132.7
N1—H1$\cdots$Br1^{i}	0.86	2.80	3.446 (4)	132.7
C2—H2$\cdots$Br1	0.93	2.90	3.516 (5)	124.7
C3—H3$\cdots$Br1^{ii}	0.93	2.99	3.699 (5)	134.2

Symmetry codes: (i) $\frac{5}{4} - x, y, \frac{1}{4} - z$; (ii) $\frac{3}{2} - x, \frac{1}{2} - y, -z$.

The data were collected at room temperature, because we observed that the crystals underwent an irreversible phase transition upon cooling. The data collection nominally covered a sphere of reciprocal space, by a combination of seven sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω. The crystal-to-detector distance was 4.0 cm. Crystal decay was monitored by repeating the initial frames at the end of data collection and analyzing the duplicate reflections.

All H atoms were located by difference Fourier synthesis and refined with fixed individual displacement parameters [U(H) = 1.5 $U_{\rm eq}$(C$_{\rm methyl}$), U(H) = 1.2 $U_{\rm eq}$(C) or U(H) = 1.2 $U_{\rm eq}$(N)] using a riding model with C—H(methyl) = 0.96, C—H(aromatic) = 0.93, or N—H = 0.86 Å, respectively.

The methyl groups attached to the aromatic ring were allowed to rotate about their local threefold axis.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART* (Siemens, 1995); data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997).

References

Adley, A. D., Bird, P. H., Fraser, A. R. & Onyszchuk, M. (1972). *Inorg. Chem.* **11**, 1402–1409.

Biradha, K., Edwards, R. E., Foulds, G. J., Robinson, W. T. & Desiraju, G. R. (1995). *J. Chem. Soc. Chem. Commun.* pp. 1705–1707.

Bryant, L. G. Jr & King, J. A. Jr (1992). *Acta Cryst.* C**48**, 2036–2039.

Bolte, M. & Kettner, M. (1998). *Acta Cryst.* C**54**, 963–964.

Chao, M., Schempp, E. & Rosenstein R. D. (1977). *Acta Cryst.* B**33**, 1820–1823.

Faber, A., Lemke, A., Spangenberg, B. & Bolte, M. (1999). *Acta Cryst.* C**55**, I*UC9900156*.

Fleischer, H., Hensen, K. & Stumpf, Th. (1996). *Chem. Ber.* **129**, 765–771.

Klebe, G., Hensen, K. & Bats, J. W. (1985). *J. Chem. Soc. Dalton Trans.* pp. 1–4.

Hensen, K., Gebhardt, F. & Bolte, M. (1998). *Acta Cryst.* C**54**, 359–361.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Siemens (1995). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Spangenberg, B. (1999). PhD thesis, University of Frankfurt, Germany.