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Tetrakis(3,5-dimethylpyridine)-dihydridosilicon dibromide bis(aceto-nitrile) solvate and 3,5-dimethyl-pyridinium bromide

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In the course of an attempt to synthesize tetrakis(3,5-dimethylpyridine)dihydridosilicon dibromide, crystals of its acetonitrile disolvate, $C_{28}H_{38}N_4Si^{2+}\cdot 2Br^-\cdot 2C_2H_3N$, (I), and of 3,5-dimethylpyridinium bromide, $C_7H_{10}N^+\cdot Br^-$, (II), were obtained in the same reaction flask. They have both been structurally characterized.

Comment

The tetrahalides of silicon, as a third period element, form interesting Lewis acid–base complexes. Addition of a Lewis base increases the coordination number of the silicon centre from four to five (Hensen *et al.*, 1982; Klebe *et al.*, 1983; Klebe, Hensen & Bats, 1983; Klebe, Hensen & Fuess, 1985; Klebe, 1985) or six (Adley *et al.*, 1972; Fleischer *et al.*, 1996). An enlargement of the coordination number to eight was shown by Carré *et al.* (1994) but, since the atomic distances are too large for such a complex, it is better to describe this complex as a complex with four covalent bonds and four intramolecular interactions between the Si and the four N atoms.

In the course of an attempt to synthesize tetrakis(3,5-dimethylpyridine)dihydridosilicon dibromide, (I), we found crystals of the 3,5-dimethylpyridinium bromide, (II), too, in the same reaction flask. The different habit of the crystals was the clue to recognizing that crystals of two different compounds had been obtained. Compound (I) is located on a crystallographic centre of inversion with half a molecule in the asymmetric unit. Bond lengths and angles do not show any unusual values. The dihedral angle between adjacent 3,5-dimethylpyridine moieties is 87.55 (8)°.

In (II), there is a hydrogen bond between the Br^- ion and the protonated N atom. Furthermore, the packing is stabilized by several C—H···halogen contacts. A comparison of the dimethylpyridine moieties in (I) and (II) shows that their geometric parameters are very similar except for the C—N—C angle, which is wider [123.5 (4)°] in (II) than in (I) [120.1 (2) and 119.8 (2)°]. The results described here demonstrate that a
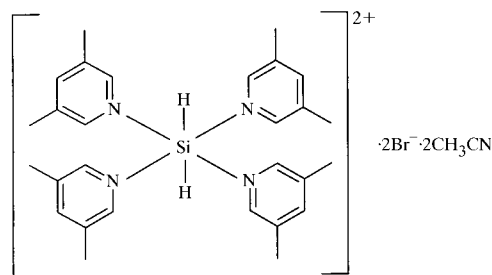
(I)
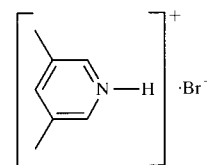
(II)

careful inspection of the whole bulk of crystals might lead to interesting results; in our case, crystals of two different compounds have formed in the same reaction flask.

Experimental

Compound (I) was prepared as described by Faber (2000). Single crystals of both title compounds were obtained from the same acetonitrile solution.

Compound (I)

Crystal data

$C_{28}H_{38}N_4Si^{2+}\cdot 2Br^-\cdot 2C_2H_3N$	$D_x = 1.327$ Mg m^{-3}
$M_r = 700.64$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 7291
$a = 9.636$ (2) Å	reflections
$b = 11.237$ (2) Å	$\theta = 1$–25°
$c = 16.242$ (3) Å	$\mu = 2.375$ mm^{-1}
$\beta = 94.49$ (1)°	$T = 173$ (2) K
$V = 1753.3$ (6) Å^3	Block, colourless
$Z = 2$	$0.75 \times 0.70 \times 0.55$ mm

Data collection

Siemens CCD three-circle diffractometer	$R_{int} = 0.056$
	$\theta_{max} = 28.28°$
ω scans	$h = -12 \rightarrow 12$
Absorption correction: empirical	$k = -14 \rightarrow 14$
(*SADABS*; Sheldrick, 1996)	$l = -21 \rightarrow 21$
$T_{min} = 0.185$, $T_{max} = 0.271$	386 standard reflections
32 839 measured reflections	frequency: 960 min
4345 independent reflections	intensity decay: none
3390 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.054$	$+ 2.4478P]$
$wR(F^2) = 0.121$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.109$	$(\Delta/\sigma)_{max} < 0.001$
4345 reflections	$\Delta\rho_{max} = 0.78$ e Å^{-3}
196 parameters	$\Delta\rho_{min} = -0.77$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C15′—H15A···Br1	0.98	2.97	3.705 (4)	133
C25′—H25A···Br1^{i}	0.98	3.19	3.850 (4)	126
C3—H3B···Br1^{i}	0.98	2.85	3.825 (4)	171
C3—H3C···Br1^{ii}	0.98	2.65	3.621 (4)	170

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

Compound (II)

Crystal data

C$_7$H$_{10}$N$^+$·Br$^-$
$M_r = 188.07$
Triclinic, $P\bar{1}$
$a = 7.504$ (2) Å
$b = 8.144$ (3) Å
$c = 8.522$ (3) Å
$\alpha = 117.80$ (1)°
$\beta = 113.43$ (1)°
$\gamma = 93.01$ (1)°
$V = 404.1$ (2) Å^3

$Z = 2$
$D_x = 1.546$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5969 reflections
$\theta = 1-25°$
$\mu = 5.002$ mm^{-1}
$T = 173$ (2) K
Needle, colourless
$0.60 \times 0.10 \times 0.10$ mm

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.153$, $T_{max} = 0.635$
9982 measured reflections
1789 independent reflections

1531 reflections with $I > 2\sigma(I)$
$R_{int} = 0.070$
$\theta_{max} = 27.10°$
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -10 \rightarrow 10$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.097$
$S = 1.097$
1789 reflections
88 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0461P)^2 + 0.3351P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.78$ e Å^{-3}
$\Delta\rho_{min} = -0.54$ e Å^{-3}

Table 2
Hydrogen-bonding geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1···Br1	0.90 (5)	2.27 (5)	3.172 (4)	175 (4)
C51—H51C···Br1^{i}	0.98	2.99	3.929 (5)	161
C2—H2···Br1^{ii}	0.95	2.84	3.749 (4)	160
C31—H31C···Br1^{ii}	0.98	3.05	3.980 (5)	160
C6—H6···Br1^{iii}	0.95	2.73	3.657 (4)	166

Symmetry codes: (i) $1 + x, y, z$; (ii) $-x, 1 - y, 1 - z$; (iii) $1 - x, 1 - y, 2 - z$.

All H atoms were located by difference Fourier synthesis and the H atoms bonded to carbon were refined with fixed individual displacement parameters [$U(H) = 1.2U_{eq}(C)$, $U(H) = 1.5U_{eq}(C_{Me})$ or $1.2U_{eq}(N)$] using a riding model with aromatic C—H = 0.95 Å or methyl C—H = 0.98 Å. H atoms bonded to silicon in (I) and hydrogen bonded to N in (II) were refined isotropically. All methyl groups of (I) and (II) were allowed to rotate about their local threefold axis.

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; 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); software used to prepare material for publication: *SHELXL*97.

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