Crystal data

$C_{10}H_{14}N_2O$
$M_r = 178.23$
Monoclinic
$P2_1/n$
$a = 8.2790(1)$ Å
$b = 13.2031(1)$ Å
$c = 9.6525(1)$ Å
$\beta = 102.852(1)°$
$V = 1028.667(18)$ Å^3
$Z = 4$
$D_x = 1.151$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 6792 reflections
$\theta = 1–25°$
$\mu = 0.076$ mm^{-1}
$T = 173$ K
Block
0.90 × 0.40 × 0.40 mm
Colourless

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: none
7842 measured reflections
2100 independent reflections
1916 reflections with $I > 2\sigma(I)$

$R_{int} = 0.019$
$\theta_{max} = 26.39°$
$h = -10 \rightarrow 10$
$k = -16 \rightarrow 16$
$l = -11 \rightarrow 12$
260 standard reflections
frequency: 1200 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.108$
$S = 1.076$
2100 reflections
119 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0493P)^2 + 0.3147P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.218$ e Å^{-3}
$\Delta\rho_{min} = -0.171$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

C2—O2	1.2143 (15)	C36—C37	1.4637 (16)
C32—C33	1.4626 (17)	C37—N38	1.1417 (16)
C33—N34	1.1371 (18)		
N34—C33—C32	178.59 (14)	N38—C37—C36	178.92 (14)
C2—C3—C31—C32	57.06 (13)	C3—C31—C32—C33	−178.38 (10)
C4—C3—C31—C32	−64.65 (13)	C31—C32—C33—N34	24 (6)
C35—C3—C31—C32	175.19 (10)	C35—C36—C37—N38	46 (7)

The data collection nominally covered over 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 5.98 cm. Coverage of the unique set is over 97% complete to at least 26° in θ. Crystal decay was monitored by repeating the initial frames at the end of data collection and analysing the duplicate reflections. H atoms were located by difference Fourier synthesis and refined with fixed individual displacement parameters $[U(\text{H}) = 1.5U_{eq}(\text{C}_{methyl})$ or $1.2U_{eq}(\text{C})]$ using a riding model with methyl C—H = 0.98 or secondary C—H = 0.99 Å. The C1 methyl group was allowed to rotate about its local threefold axis.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1367). Services for accessing these data are described at the back of the journal.

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3,3′-(1-Silacyclohexane-1,1-diyl)bis(1-methylimidazolium) Dibromide Acetonitrile Solvate at 173 K

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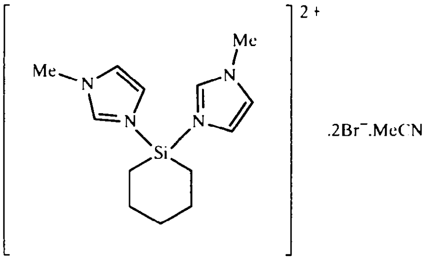
Abstract

The title compound, $C_{13}H_{22}N_4Si^{2+}.2Br^-.C_2H_3N$, crystallizes from the solution of *N*-methylimidazole and 1,1-dibromosilacyclohexane in which it was prepared. Two Br^- ions of the starting material are removed from the first area of coordination of the Si atom. The resulting species is a dication. The structure displays a six-membered silaheterocycle containing a tetracoordinated Si atom. The crystal was a racemic twin.

Comment

Recently, we reported the synthesis and structure determination of tetrakis(*N*-methylimidazole)silacyclopentane dichloride (Hensen *et al.*, 1997), the first Lewis acid–base adduct consisting of a silaheterocycle and *N*-methylimidazole (NMI). However, the homologous

1,1-dichlorosilacyclohexane does not form an adduct with NMI. Now, we have found that the reaction of 1,1-dibromosilacyclohexane with NMI in acetonitrile leads to a 1:2 adduct, (I).



(I)

The asymmetric unit contains a six-membered sila-heterocycle bearing two NMI ligands, two Br^- ions and one solvent molecule. The silaheterocycle exhibits a chair conformation, slightly flattened in the region of Si1. The Si atom is tetracoordinated. The two Br^- ions are displaced from the first area of coordination by the NMI molecules. The Si—N distances [Si1—N11 1.783 (8) and Si1—N21 1.779 (7) Å] are nearly equal. They are also comparable to the Si—N bond distance [1.791 (4) Å] found in $[Me_2Si(NMI)_2]Br_2$ (Burger *et al.*, 1995), which is also a dicationic tetracoordinated silicon Lewis acid–base adduct. A search of the Cambridge Structural Database (Allen & Kennard, 1993) revealed only one comparable structure (Engelhardt & Rosefid, 1994), where the Si—N bonding is covalent and has distances 1.760 (4) and 1.761 (3) Å, only slightly shorter than the dative bond in the title compound. The N—Si—N angle in the title compound is 100.4 (4)°, which is markedly smaller than in $[Me_2Si(NMI)_2]Br_2$ [105.3 (2)°].

The Br^- ions are involved in six H···Br contacts that may be interpreted as C—H···Br hydrogen bonds (Table 2).

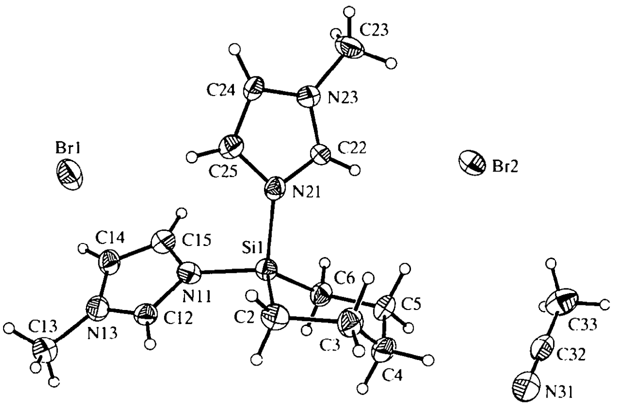


Fig. 1. Perspective view of the title compound with the atom numbering; displacement ellipsoids are at the 50% probability level.

Experimental

In order to avoid atmospheric humidity, the preparative work was carried out under an inert atmosphere, *i.e.* N_2 or Ar. The NMI was refluxed from CaH_2 and then distilled. Acetonitrile was dried using a 3 Å molecular sieve. The preparation of 1,1-dibromosilacyclohexane followed the procedure of Ackermann *et al.* (1980). To prepare the adduct, slightly more than two equivalents of NMI were added to a solution of 1,1-dibromosilacyclohexane (4.1 mmol) in acetonitrile (20 ml). Single crystals were obtained from this solution by slow evaporation of the solvent.

Crystal data

$C_{13}H_{22}N_4Si^{2+}.2Br^-.C_2H_3N$
$M_r = 463.31$
Orthorhombic
$Pna2_1$
$a = 11.0034\ (2)$ Å
$b = 27.2848\ (4)$ Å
$c = 6.7194\ (1)$ Å
$V = 2017.34\ (6)$ Å^3
$Z = 4$
$D_x = 1.525$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 7038 reflections
$\theta = 1–25°$
$\mu = 4.084$ mm^{-1}
$T = 173$ K
Block
0.40 × 0.30 × 0.20 mm
Colourless

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.260$, $T_{max} = 0.442$
9668 measured reflections
3546 independent reflections

3174 reflections with $I > 2\sigma(I)$
$R_{int} = 0.046$
$\theta_{max} = 26.17°$
$h = -12 \rightarrow 13$
$k = -33 \rightarrow 32$
$l = -8 \rightarrow 7$
211 standard reflections
frequency: 540 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.065$
$wR(F^2) = 0.172$
$S = 1.010$
3546 reflections
212 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.1038P)^2 + 11.0438P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.057$
$\Delta\rho_{max} = 3.124$ e Å^{-3}
$\Delta\rho_{min} = -0.792$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Si1—N11	1.783 (8)	Si1—C2	1.822 (10)
Si1—N21	1.779 (7)	Si1—C6	1.837 (10)
N11—Si1—N21	100.4 (4)	N11—Si1—C6	116.2 (4)
N11—Si1—C2	107.8 (4)	N21—Si1—C6	109.2 (4)
N21—Si1—C2	113.0 (4)	C2—Si1—C6	110.1 (5)
Si1—C2—C3—C4	57.2 (10)	C4—C5—C6—Si1	−47.6 (10)
C2—C3—C4—C5	−69.6 (11)	C5—C6—Si1—C2	40.3 (8)
C3—C4—C5—C6	63.8 (11)	C6—Si1—C2—C3	−44.4 (8)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D* H···*A*
C25—H25···Br1	0.95	2.69	3.639 (9)	173.5
C14—H14···Br1^{i}	0.95	2.91	3.857 (10)	173.1
C24—H24···Br1^{ii}	0.95	2.75	3.673 (8)	163.0
C12—H12···Br1^{iii}	0.95	2.81	3.704 (10)	156.8
C22—H22···Br2	0.95	2.90	3.768 (8)	153.2
C15—H15···Br2^{iv}	0.95	2.84	3.711 (10)	152.6

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

The data collection nominally covered over a sphere of reciprocal space, by a combination of three 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 6.0 cm. Coverage of the unique set is over 96% complete to at least 25° in θ, regarding Friedel opposites as distinct. Crystal decay was monitored by repeating the initial frames at the end of data collection and analysing the duplicate reflections. All H atoms could be located by difference Fourier synthesis and were refined with fixed individual displacement parameters [$U(\text{H}) = 1.5U_{eq}(\text{C}_{methyl})$ or $U(\text{H}) = 1.2\ U_{eq}(\text{C})$], using a riding model with methyl C—H = 0.98, aromatic C—H = 0.95 or secondary C—H = 0.99 Å. The methyl groups were allowed to rotate about their local threefold axis. The final electron-density map shows one peak of 3.124 eÅ^{-3} at a distance of 0.97 Å from Br2, probably attributable to residual absorption errors. The crystal was a racemic twin, and the ratio of the twin components refined to 0.58 (2):0.42(2).

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). Molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1295). Services for accessing these data are described at the back of the journal.

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3-[(2-Bromo-4-methylphenyl)iminomethyl]-2-hydroxy-5-methylbenzaldehyde

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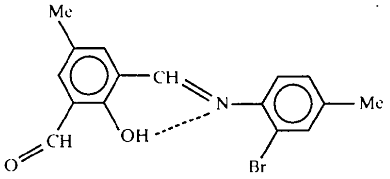
Abstract

Molecules of the title compound, $C_{16}H_{14}BrNO_2$, are almost planar. Each contains a strong intramolecular N···H—O hydrogen bond between the imine and hydroxyl groups [N···O 2.574 (5) Å].

Comment

Schiff base compounds can be classified by their photochromic and thermochromic characteristics in the solid state by proton transfer from the hydroxyl O atom to the imine N atom (Cohen *et al.*, 1964). The charge transport occurs through overlapping intramolecular π orbitals with proton transfer (Hadjoudis *et al.*, 1987). Proton transfer could also provide the basis for molecular switches (Xu *et al.*, 1994). In the course of a systematic structural investigation of Schiff bases (Elerman *et al.*, 1991, 1992, 1994, 1995, 1997; Elerman, Kabak, Elmali & Svoboda, 1998; Elerman & Elmali, 1998; Elerman, Elmali, Svoboda & Fuess, 1998; Elmali *et al.*, 1995; Elmali & Elerman, 1997, 1998; Elmali, Elerman & Zeyrek, 1998; Elmali, Elerman & Kendi, 1998), the structure of the title compound, (I), was determined.



(I)

From some thermochromic and photochromic Schiff base compounds, it was proposed that molecules exhibiting thermochromic properties are planar, while those exhibiting photochromic properties are non-planar (Moustakali-Mavridis *et al.*, 1978). In agreement with the conclusions above, the title molecule is ther-