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Dynamic disorder in a pentacoordinate silicon complex with 2,2′-diazenediyldiphenol

Uwe Böhme* and Sandra Jähnigen

Institut für Anorganische Chemie, Technische Universität Bergakademie Freiberg, Leipziger Strasse 29, 09596 Freiberg, Germany
Correspondence e-mail: uwe.boehme@chemie.tu-freiberg.de

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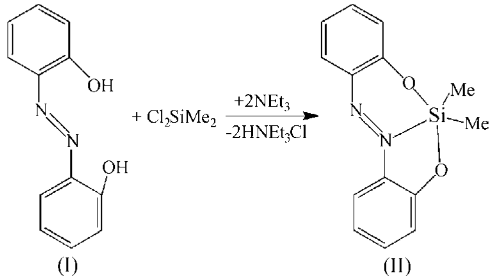
The crystal structure of (2,2′-diazenediyldiphenolato-κ^3O,N,O')-dimethylsilicon, $C_{14}H_{14}N_2O_2Si$, determined at four temperatures, reveals a dynamic disorder as a result of a flipping of the orientation of the C—N=N—C unit. The population of the two conformers in the single crystal depends on the temperature and cooling rate. It is possible to minimize the disorder by cooling the crystal slowly.

Comment

The chemistry of hypercoordinate silicon complexes is currently one of the main research areas in silicon chemistry (Chuit *et al.*, 1993; Corriu & Young, 1989; Holmes, 1996; Kost & Kalikhman, 1998, 2004; Pestunovich *et al.*, 1998; Tacke *et al.*, 1999). During our work on penta- and hexacoordinate silicon complexes with *O*,*N*,*O*′-tridentate ligands (Böhme *et al.*, 2006; Böhme & Günther, 2007; Böhme & Foehn, 2007), we used 2,2′-diazenediyldiphenol, (I), as a potential ligand molecule. The reaction of (I) with dichlorodimethylsilane in the presence of triethylamine in tetrahydrofuran (THF) yields, after work-up, a red crystalline product. The X-ray crystal structure analysis of a suitable crystal at room temperature verified the formation of the title pentacoordinate silicon complex, (II) (Fig. 1).



(I) (II)

In (II), the Si atom is bound to the C atoms of the methyl groups (atoms C13 and C14) and to the two O atoms and one of the N atoms of the 2,2′-diazenediyldiphenolate ligand. There is disorder in the structure as a result of a flipping of the orientation of the C—N=N—C unit. Essentially, the 2,2′-diazenediyldiphenolate ligand is superimposed on a mirror image of itself in the plane bisecting the C1$\cdots$C7 line (Fig. 1). Thus, all atoms of the 2,2′-diazenediyldiphenolate ligand are expected to be disordered, but only the N and O atoms could be modelled successfully as disordered (see *Experimental*). The occupancy of the minor conformation is 17.4 (3)%. An attempt was made to diminish the disorder by cooling the crystal to 153 K over a period of 1 h. After a fresh data collection, the minor disordered component in the crystal was estimated to be 4.1 (2)%. This result points to the presence of dynamic disorder. The crystal – having been warmed to room temperature – was then flash-cooled to 93 K. The subsequent X-ray structure analysis shows in this case that the disorder is nearly identical to that in the sample measured at room temperature [13.4 (3)%]. The possibility of observing unstable conformers in flash-cooled crystals has been demonstrated previously (Harada & Ogawa, 2004). The crystal was warmed again to room temperature and then cooled slowly within 2 h to 93 K. The fourth determination of the crystal structure shows that the minor component of the disorder is reduced to a minimum proportion of 4.1 (2)%. All four crystal structure determinations were performed with the same crystal, and the crystal was warmed to room temperature between every measurement.

The best results were seen for the structure determination at 153 K (Fig. 2) and some of the main geometric features of

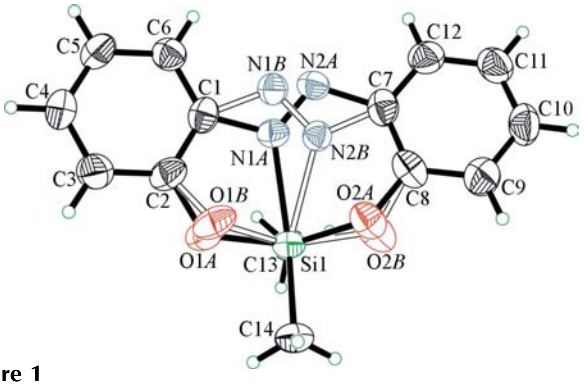


Figure 1
The molecular structure of (II) at room temperature (298 K), showing the 17.4 (5)% disorder (open bonds). Displacement ellipsoids are drawn at the 50% probability level.

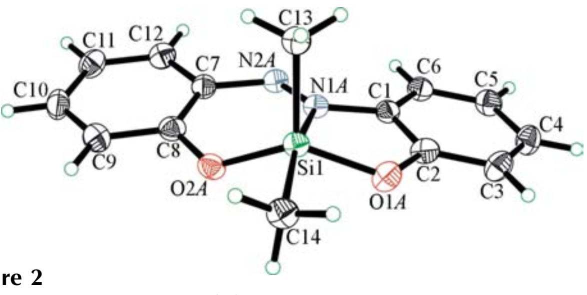


Figure 2
The molecular structure of (II) at 153 K. The minor disorder component [4.1 (5)%] has been omitted. Displacement ellipsoids are drawn at the 50% probability level.

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the structure at this temperature are as follows. The Si—O distances [Si1—O1*A* = 1.7136 (12) Å and Si1—O2*A* = 1.7014 (12) Å] are short but comparable to those of similar compounds (Böhme & Günther, 2007). The Si—C distances are in the usual range [Si1—C13 = 1.8594 (15) Å and Si1—C14 = 1.8684 (15) Å]. The Si—N distances are longer than expected [Si1—N1*A* = 2.1666 (13) Å and Si1—N2*B* = 2.172 (5) Å], which is easily explained by the coordinative character of this bond. One might think that 95.9 (5)% site occupation is not really distinguishable from 100%. However, if the structure of (II) at 153 K is refined without treatment of the disorder, the *R* value rises from 0.0384 to 0.0406 and the residual density map (Fig. 3) shows sharp peaks of residual electron density for the disordered N atoms and smaller peaks for the rest of the 2,2′-diazenediyldiphenolate ligand.

Dynamic disorder has often been observed in azobenzene and stilbene derivatives (Bernstein, 1975; Borbulevych & Antipin, 2001; Harada *et al.*, 1997; Harada & Ogawa, 2004). Surprisingly, it was now detected in the silicon complex (II). The mechanism of rearrangement in the solid state has been explained with a 'pedal motion' (Harada *et al.*, 1997). The energy necessary to perform such a 'pedal motion', *i.e.* the rotation of the –N═N– unit, for one single molecule of (II) in the gas phase has been calculated at the B3LYP/6–31G(d,p) level with a free enthalpy of 55.4 kJ mol^{-1}. The geometry of the calculated transition state is shown in Fig. 4. Another mechanism of rearrangement would be the inversion of the SiMe$_2$ group. This inversion has an activation energy of only 8.0 kJ mol^{-1} in free enthalpy [B3LYP/6–31G(d,p)], which is easily possible in solution but is unlikely to take place in the crystalline state.

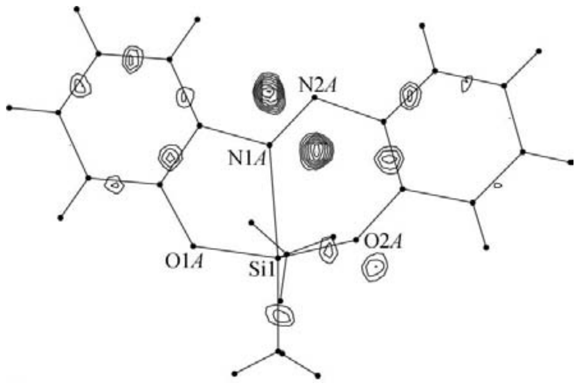

Figure 3
A residual electron-density map of (II) at 153 K in the O1*A*/N1*A*/N2*A*/O2*A* plane after refinement without disordered atoms. The first contour is at 0.6 e Å^{-3} and the contour levels are at 0.05 e Å^{-3}.

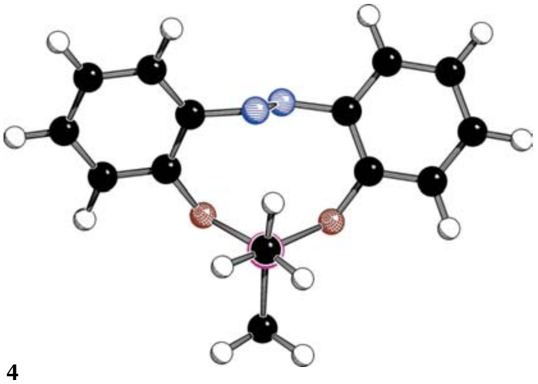

Figure 4
The calculated geometry of the transition state for the 'pedal motion' rearrangement of (II).

To interpret the results of the crystal structure determinations one can say the following: if there is a crystalline sample that raises suspicion of dynamic disorder, it is useful to cool the sample slowly. Flash-cooling or quick-freezing, as is often practiced in routine crystallographic work, is not the best approach in every case. Of course, we are aware that there is not always enough time to make a number of different structure determinations from a given crystal, but in some cases it might help to keep these conclusions in mind during daily crystallographic practice.

Experimental

The preparation of (II) was performed in Schlenk tubes under argon with dry and air-free solvents. Me$_2$SiCl$_2$ (0.84 g, 0.0065 mol) and triethylamine (1.46 g, 0.0144 mol) were dissolved in THF (80 ml) and cooled to 273 K. 2,2′-Diazenediyldiphenol (1.4 g, 0.0065 mol) was dissolved in THF (60 ml) and added dropwise to the stirred mixture of Me$_2$SiCl$_2$ and triethylamine. A precipitate was formed immediately and the mixture became red. After removal of the cooling bath, the mixture was stirred at room temperature for 70 h. The suspension was filtered into a Schlenk tube and the remaining solid, which is NEt$_3$HCl, was washed with small amounts of THF. The solvent was completely removed *in vacuo* and the red residue was recrystallized from 1,2-dimethoxyethane (yield 1.4 g, 79.7%; m.p. 388 K). Crystals suitable for X-ray structure analysis were obtained by recrystallization from diethyl ether. Analysis calculated for $C_{14}H_{14}N_2O_2Si$: C 62.20, H 5.22, N 10.36%; found: C 62.08, H 5.18, N 10.53%. ^{29}Si NMR (CDCl$_3$): δ −50.2; ^{1}H NMR (CDCl$_3$): δ 0.15 (*s*, Me, 6H), 7.0–7.5 (*m*, Ph, 8H); ^{13}C NMR (CDCl$_3$): δ 1.7 (Me), 120.5, 121.5, 123.3, 134.5, 138.2, 152.6 (six signals for Ph).

Compound (II) at 298 K

Crystal data

$C_{14}H_{14}N_2O_2Si$
$M_r = 270.36$
Orthorhombic, *Pbca*
$a = 10.2295$ (2) Å
$b = 8.0212$ (1) Å
$c = 32.1141$ (5) Å
$V = 2635.05$ (7) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.18$ mm^{-1}
$T = 298$ (2) K
0.45 × 0.18 × 0.15 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.921$, $T_{\max} = 0.978$
36746 measured reflections
3192 independent reflections
2533 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.144$
$S = 1.11$
3192 reflections
211 parameters
64 restraints
H-atom parameters constrained
$\Delta\rho_{\max} = 0.41$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}

Compound (II) at 153 K

Crystal data

$C_{14}H_{14}N_2O_2Si$
$M_r = 270.36$
Orthorhombic, *Pbca*
$a = 10.0440\ (11)$ Å
$b = 7.8990\ (8)$ Å
$c = 32.011\ (3)$ Å
$V = 2539.7\ (4)$ Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.18$ mm^{-1}
$T = 153\ (2)$ K
0.45 × 0.18 × 0.15 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.921$, $T_{\max} = 0.978$
16295 measured reflections
3063 independent reflections
2632 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.103$
$S = 1.08$
3063 reflections
211 parameters
64 restraints
H-atom parameters constrained
$\Delta\rho_{\max} = 0.36$ e Å^{-3}
$\Delta\rho_{\min} = -0.35$ e Å^{-3}

Compound (II) at 93 K (flash cooled)

Crystal data

$C_{14}H_{14}N_2O_2Si$
$M_r = 270.36$
Orthorhombic, *Pbca*
$a = 10.0654\ (5)$ Å
$b = 7.9069\ (4)$ Å
$c = 31.9971\ (17)$ Å
$V = 2546.5\ (2)$ Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.18$ mm^{-1}
$T = 93\ (2)$ K
0.45 × 0.18 × 0.15 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.921$, $T_{\max} = 0.978$
13356 measured reflections
2937 independent reflections
2606 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.022$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.094$
$S = 1.04$
2937 reflections
211 parameters
64 restraints
H-atom parameters constrained
$\Delta\rho_{\max} = 0.44$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}

Compound (II) at 93 K (slow cooled)

Crystal data

$C_{14}H_{14}N_2O_2Si$
$M_r = 270.36$
Orthorhombic, *Pbca*
$a = 10.0248\ (10)$ Å
$b = 7.8879\ (8)$ Å
$c = 32.162\ (3)$ Å
$V = 2543.2\ (4)$ Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.18$ mm^{-1}
$T = 93\ (2)$ K
0.45 × 0.18 × 0.15 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.921$, $T_{\max} = 0.978$
11554 measured reflections
2341 independent reflections
2116 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.022$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.085$
$S = 1.10$
2341 reflections
211 parameters
64 restraints
H-atom parameters constrained
$\Delta\rho_{\max} = 0.38$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}

Evidence was found for disorder of the 2,2′-diazenediyldiphenolate ligand, as discussed in the *Comment*. It would be desirable to define two positions for all atoms of the 2,2′-diazenediyldiphenolate ligand, since the benzene rings must have disordered orientations as well (*cf* Fig. 3 and geometrical considerations). However, such a treatment of the structure model makes the refinement unstable. As a compromise, only the N and O atoms were treated with a split-atom model. This model reflects the major aspects of the disorder and allows the disorder to be treated in the same way in all four structure determinations. Adjacent disordered atoms have been restrained to have similar U^{ij} components and the lengths of chemically equivalent bonds involving at least one disordered atom were also restrained to be similar. All H atoms were positioned geometrically and were allowed to ride on their parent atoms, with C—H distances of 0.93–0.98 Å and $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(C) or $1.5U_{\rm eq}$(methyl C).

For all compounds, data collection: *SMART* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3102). Services for accessing these data are described at the back of the journal.

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