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Pentacoordination *versus* tetracoordination in silicon derivatives of an *O,N,O′*-tridentate ligand[1]

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Bis[2-(2-hydroxy-3-methoxybenzylideneamino)phenolato-κO]-dimethylsilicon, $C_{30}H_{30}N_2O_6Si$, (II), was isolated from the reaction of 2-(2-hydroxy-3-methoxybenzylideneamino)phenol, (I), with dichlorodimethylsilane at 339 K. It consists of two ligand molecules and the Me_2Si unit forming a dialkoxydimethylsilane with a tetracoordinate Si atom. [2-(3-Methoxy-2-oxidobenzylideneamino)phenolato-$\kappa^3 O,N,O′$]dimethylsilicon, $C_{16}H_{17}N$-O_3Si, (III), was isolated from the same reaction conducted at 263 K. In this complex, the dianion of (I) is coordinated *via* two O atoms and an azomethine N atom to the pentacoordinate Si atom. According to quantum chemical calculations, (II) is the thermodynamically stable product and (III) is the kinetically favoured product.

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). In 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-hydroxy-3-methoxybenzylideneamino)phenol, (I), as a potential ligand molecule. The reaction of (I) with dichlorodimethylsilane in the presence of triethylamine in tetrahydrofuran under reflux conditions yields product mixtures, as shown by a ^{29}Si NMR spectrum of the reaction solution. Extraction with *n*-hexane was attempted during the work-up procedure. The raw product shows poor solubility in the nonpolar solvent. The hexane solution was decanted from the product mixture, the solvent was removed *in vacuo* and the residue was recrystallized from a hexane/chloroform mixture (3:1 *v/v*) and stored for several weeks at 258 K. During that time an orange crystal formed. X-ray crystal structure analysis shows the formation of (II) as an unexpected side product

from this reaction [Fig. 1 and reaction (*a*) in the Scheme]. Two ligand molecules and the Me_2Si unit form a dialkoxydimethylsilane with a tetracoordinate Si atom. The Si—O bonds [Si1—O2 = 1.654 (1) Å and Si1—O5 = 1.650 (1) Å] and the Si—C bonds [Si1—C29 = 1.842 (2) Å and Si1—C30 = 1.837 (2) Å] are typical for compounds of this type (Kaftory *et al.*, 1998). The coordination geometry at the Si atom is distorted tetrahedral with bond angles between 104.50 (7) (O5—Si1—C30) and 116.2 (1)° (C30—Si1—C29). The compound is further stabilized by two intramolecular O—H⋯N hydrogen bonds between the *ortho*-hydroxy groups and the azomethine N atoms (see Table 2). Repeated attempts to prepare compound (II) selectively by choosing the appropriate ratio of reagents failed.
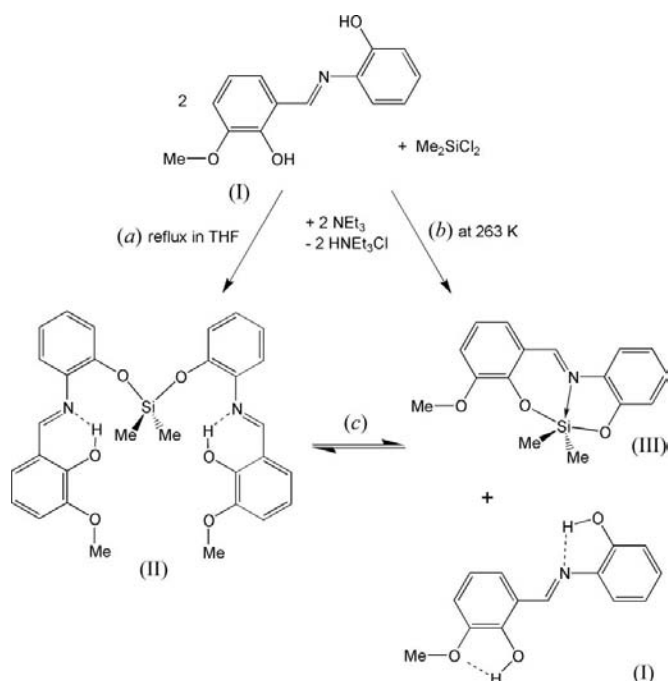
On the other hand, it was possible to obtain the desired pentacoordinate product by choosing suitable reaction conditions [Scheme, reaction (*b*)]. The reaction between (I) and dichlorodimethylsilane was carried out at 263 K with a short reaction time (0.5 h) followed by immediate work-up of the reaction batch. A red crystalline product was obtained after work-up. The X-ray crystal structure analysis of a suitable crystal verified the formation of the pentacoordinate Si complex, (III) (Fig. 2). The Si atom is bound to the C atoms of the methyl groups (C15 and C16), to the O atoms (O1 and O2) and to the N atom (N1) of a single imine ligand. The Si—O [Si1—O1 = 1.7125 (9) Å and Si1—O2 = 1.367 (9) Å] and the Si—C distances [Si1—C15 = 1.872 (1) Å and Si1—C16 = 1.882 (1) Å] are comparable with those in similar pentacoordinate compounds (Böhme & Günther, 2007). The Si—N distance is longer [Si1—N1 = 2.068 (1) Å], which is easily explained by the coordinative character of this bond. The coordination geometry at the Si atom can be deduced from the bond angles at the Si atom. A suitable parameter for the description of the coordination geometry in pentacoordinate complexes is defined as $\tau = (\beta - \alpha)/60$ (Addison *et*

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[1] Dedicated to Professor K.-H. Thiele on the occasion of his 80th birthday.
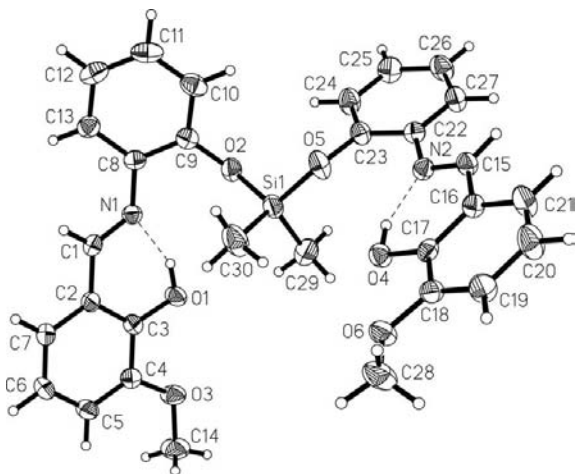
Figure 1
The molecular structure of (II) at 153 K shown with 50% probability displacement ellipsoids. Dashed lines indicate intramolecular hydrogen bonds.

Figure 2
The molecular structure of (III) at 153 K shown with 50% probability displacement ellipsoids.

al., 1984). Angle β is the largest angle at the central atom and angle α is the second largest. For a perfect square pyramid, τ is equal to zero, whereas it becomes one for a perfect trigonal bipyramid. The two largest bond angles at Si in (III) are O1—Si—O2 = 135.57 (5)° and C16—Si1—N1 = 163.39 (6)°. This gives a value of $\tau = 0.46$ for complex (III), which indicates an intermediate coordination geometry. If we were to consider (III) as a strongly distorted square pyramid, the apex of the pyramid would be formed by atom C15, while atoms O1, O2, N1 and C16 would represent the base of the pyramid. The coordination geometry of (III) is far more distorted than the geometries of comparable Si complexes with 2-{1-[(2-hydroxyethyl)imino]ethyl}phenol as the *O,N,O'*-tridentate ligand. Complexes with this ligand have τ values from 0.78 (Böhme & Günther, 2007) to 0.94 (Böhme & Foehn, 2007) as a result of a more flexible ethylene group instead of the phenylene group used in (III). The ethylene group allows for the occurrence of a relaxed coordination geometry close to that of an ideal trigonal bipyramid.

Bond lengthening through higher coordination is a known effect in silicon chemistry (Chuit *et al.*, 1993), and it is interesting to compare the bond lengths of the pentacoordinate derivative, (III), with the bond lengths of the tetracoordinate compound, (II). The Si1—O2 bond in (III) is 4.8 and 5.0% longer, respectively, than the comparable Si1—O2 and Si1—O5 bonds in (II). The average value of the Si—C bonds in (III) is 2% longer than the average of the Si—C bonds in (II).

It is possible to explain the preferred formation of a product mixture containing (II) on the basis of quantum chemical calculations. The geometries of (II), (III) and four different conformations of the ligand molecule (I) have been optimized with B3PW91/6–31G(d,p). If we assume an equilibrium between (II) and a mixture of (I) and (III) [equilibrium (*c*) in the Scheme], we can calculate the enthalpy ($\Delta_R H$) and free energy ($\Delta_R G$) for this reaction (see Table 4). The most stable conformation of (I) which was used for calculating the energy values in Table 4 is shown at the bottom of the Scheme. According to the quantum chemical analysis, the enthalpy of
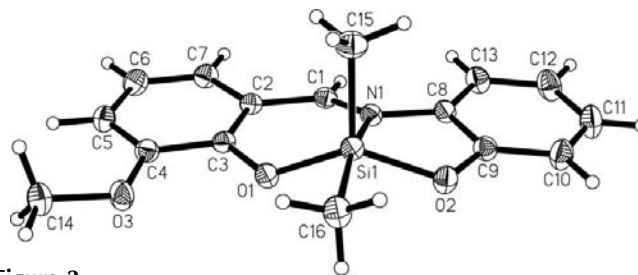
(II) is 42.3 kJ mol^{-1} lower than the sum of the enthalpies of (I) and (III). That means an individual molecule of (II) is thermodynamically more stable at 0 K than the mixture of (I) and (III). This picture becomes diversified if we consider the entropy of the system, which is 0.14 kJ mol^{-1} K^{-1}, and calculate the free energy. The difference in free energy is only 1.6 kJ mol^{-1} at 298 K. Thus, at room temperature, (II) is only marginally lower in energy than the mixture of (I) and (III). Raising the temperature above 298 K leads to a free energy of nearly zero ($\Delta_R G \simeq 0$), *i.e.* the compounds (II), (III) and (I) are in equilibrium. This explains the formation of product mixtures during the syntheses under reflux conditions.

The synthesis at low temperatures favours the formation of (III), which therefore should be considered as the kinetically preferred product if we take into consideration the competition between reactions (*a*) and (*b*). The influence of solvents, the solubility of intermediates and products, and the varying ratio of starting materials are not accounted for in this quantum chemical analysis and would complicate the situation further.

The isolation of (II) and (III) from the same starting materials represents a rare case, which allows insight into the complicated interplay between thermodynamic and kinetic factors determining the formation of tetra- or penta-coordinated compounds of silicon.

Experimental

Compounds (II) and (III) were prepared in Schlenk tubes under an argon atmosphere with anhydrous and air-free solvents.

For the preparation of (II), product mixtures were obtained when the reaction of 2-(2-hydroxy-3-methoxybenzylideneamino)phenol, (I), with dichlorodimethylsilane was performed in tetrahydrofuran (THF) under reflux. The composition of the reaction mixture was analysed by ^{29}Si NMR. The reaction mixture was filtered over a Schlenk filter and the residue was washed with THF. The solvent was removed completely *in vacuo*. Subsequent extraction of the red oily residue with hexane and diethyl ether also yielded product mixtures. The hexane was removed *in vacuo* from the extracted solution. Recrystallization from a hexane/chloroform mixture (3:1 *v/v*) gave one orange crystal of (II), which was characterized by X-ray structure analysis. Further spectroscopic characterization was not possible since only one crystal of (II) was obtained.

For the preparation of (III), (I) (1.50 g, 6.2 mmol) was dissolved in THF (70 ml) and triethylamine (1.87 g, 18.5 mmol, 50% excess) was added with a syringe. The reaction mixture was cooled to 263 K. After a few minutes, dichlorodimethylsilane (0.84 g, 6.5 mmol, 5%

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excess) was added with a syringe and this reaction mixture was stirred for 0.5 h at 263 K. After that time, a red suspension had formed. The suspension was filtered over a G3 filter at room temperature and the residue was washed with THF (3×10 ml). The solvent was removed completely from the red filtrate *in vacuo*. The residue was dissolved in chloroform (5 ml), and *n*-hexane (8 ml) was added. A red crystalline precipitate deposited. The precipitate was filtered off, washed with *n*-hexane (2×2 ml) and dried *in vacuo*; red prisms (1.23 g, 67%, m.p. 416–419 K). ^{1}H NMR (CDCl$_3$): δ 8.63 (*s*, CH=N), 7.37–6.82 (*m*, CH$_{ar}$), 3.89 (*s*, OCH$_3$), 0.33 (*s*, Si—CH$_3$). ^{13}C NMR (CDCl$_3$): δ 155.9 (C1), 154.7 (C4), 152.2 (C9), 151.0 (C3), 131.1, 130.7, 123.5, 119.5, 118.9, 118.8, 118.1, 116.0, 113.6 (nine signals C$_{ar}$), 56.6 (C14), 3.6 (C15 and C16). ^{29}Si NMR (CDCl$_3$): δ −59.2.

Compound (II)

Crystal data

C$_{30}$H$_{30}$N$_2$O$_6$Si	$V = 2843.5\ (2)$ Å^3
$M_r = 542.65$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 16.5171\ (8)$ Å	$\mu = 0.13$ mm^{-1}
$b = 10.4952\ (5)$ Å	$T = 153$ K
$c = 18.2931\ (9)$ Å	$0.52 \times 0.50 \times 0.38$ mm
$\beta = 116.272\ (1)°$	

Data collection

Bruker SMART CCD area-detector diffractometer	39389 measured reflections
	6204 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) $T_{min} = 0.932$, $T_{max} = 0.956$	4889 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.100$	
$S = 1.07$	
6204 reflections	$\Delta\rho_{max} = 0.35$ e Å^{-3}
364 parameters	$\Delta\rho_{min} = -0.33$ e Å^{-3}

Table 1
Selected bond angles (°) for (II).

O5—Si1—O2	109.28 (6)	O5—Si1—C29	110.53 (7)
O5—Si1—C30	104.50 (7)	O2—Si1—C29	104.76 (7)
O2—Si1—C30	111.53 (7)	C30—Si1—C29	116.2 (1)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H3$\cdots$N1	0.89 (2)	1.77 (2)	2.600 (2)	153 (2)
O4—H17$\cdots$N2	0.93 (2)	1.68 (2)	2.540 (2)	152 (2)

Compound (III)

Crystal data

C$_{16}$H$_{17}$NO$_3$Si	$V = 1495.61\ (10)$ Å^3
$M_r = 299.40$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 9.0207\ (3)$ Å	$\mu = 0.17$ mm^{-1}
$b = 12.8134\ (5)$ Å	$T = 153$ K
$c = 12.9427\ (5)$ Å	$0.40 \times 0.34 \times 0.32$ mm
$\beta = 91.303\ (2)°$	

Table 3
Selected bond angles (°) for (III).

O1—Si1—O2	135.57 (5)	C15—Si1—C16	105.83 (7)
O1—Si1—C15	111.80 (6)	O1—Si1—N1	84.87 (4)
O2—Si1—C15	110.10 (6)	O2—Si1—N1	80.52 (4)
O1—Si1—C16	90.48 (5)	C15—Si1—N1	90.68 (5)
O2—Si1—C16	91.88 (5)	C16—Si1—N1	163.39 (6)

Table 4
Calculated enthalpy and free energy for (II) and (III) plus (I) at the B3PW91/6–31G(d,p) level of theory.

Total enthalpies and free energies are given in Hartree. All molecule geometries have been optimized and the stationary points were verified by calculating the Hessian matrices.

Molecule	Enthalpy	Free energy at 298 K
(III) plus (I)	−2010.424566	−2010.553834
(II)	−2010.440665	−2010.554451
Difference in Hartree	0.016099	0.000617
Difference in kJ mol^{-1}	42.3	1.6

Data collection

Bruker SMART CCD area-detector diffractometer	17497 measured reflections
	3975 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) $T_{min} = 0.932$, $T_{max} = 0.950$	3463 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.109$	
$S = 1.05$	
3975 reflections	$\Delta\rho_{max} = 0.36$ e Å^{-3}
197 parameters	$\Delta\rho_{min} = -0.29$ e Å^{-3}

The two H atoms in (II) forming the hydrogen bonds between the phenolic O and azomethine N atoms and the H atom at C1 in (III) were located in difference Fourier maps, and their positions and isotropic displacement parameters were refined. All other H atoms were positioned geometrically and were allowed to ride on their parent atoms, with C—H = 0.95 (phenyl) or 0.98 Å (methyl) and with U_{iso}(H) = $1.2U_{eq}$(phenyl C) or $1.5U_{eq}$(methyl C).

For both compounds, data collection: *SMART* (Bruker, 2007); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2007); 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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