Two modifications of a five-coordinate silicon complex

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TBPY-5-34-(Butane-1,4-diyl)(2-{[1-(2-oxidophenyl)ethylidene-κO]amino-κN}ethanolato-κO)silicon, $C_{14}H_{19}NO_2Si$, crystallizes in two modifications. The monoclinic form, (IIm), was obtained by crystallization over a period of 2 d at room temperature; the orthorhombic form, (IIo), crystallized overnight at 248 K. The main difference between the two molecular structures involves the angles in the equatorial plane of the trigonal bipyramid around silicon. Form (IIm) has an O—Si—O angle of ca 121° and O—Si—C angles of ca 121 and 116°. In form (IIo), the corresponding angles are ~123, 124 and 111°. There are also significant differences in the packing: (IIm) shows π stacking, whereas (IIo) does not.

Comment

Silicon complexes with tridentate Schiff base ligands and O,N,O'-coordination modes are known, having been prepared by various groups (Prasad & Tandon, 1973; Abe *et al.*, 1986; Singh & Singh, 1987; Koacher *et al.* 1980). A number of applications of these complexes have been proposed and described. Investigations have focused on photovoltaic applications (Nagao *et al.*, 2004), colouring materials (Nagao *et al.*, 2002; Misono *et al.*, 1985, 1987), antimicrobial activity (Nath & Goyal, 2002) and use as electrophotographic toner (Yamanaka & Sugawara, 1991). The existence of polymorphs is of importance for many applications that depend on the solid-state properties of a given compound (Bernstein, 2003; Hilfiker, 2006). We report here the dimorphic solid-state structures of the title compound, (II).
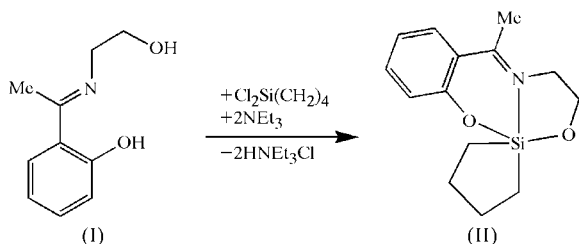
The reaction of 2-aminoethanol with *o*-hydroxyaceto-phenone gives facile access to a Schiff base ligand, (I), with

O,N,O'-coordination ability. The reaction of this ligand with 1,1-dichlorosilacyclopentane in the presence of triethylamine yields the desired silicon complex (II), which was characterized by NMR spectroscopy. The ^{29}Si NMR chemical shift at −53.15 p.p.m. indicates the formation of a five-coordinate silicon complex. A saturated solution of the reaction product was left standing for two days at room temperature. During this time, large clear colourless hexagonal prisms were formed from the pale-yellow solution. Investigation of several crystals from this crystallization batch showed the formation of monoclinic crystals (space group $P2_1/c$), which are denoted here as (IIm). Fig. 1 shows the molecular structure of (IIm) and the atomic labelling scheme. Selected bond lengths and angles are listed in Table 1.

The remaining solution was separated from this first batch and left overnight at 248 K in a freezer. Another crystalline fraction was formed consisting of small colourless prisms with a rectangular shape. Investigation of the cell constants of several crystals from this crystallization batch showed, surprisingly, the exclusive formation of orthorhombic crystals, denoted (IIo). The orthorhombic dimorph crystallizes in the chiral space group $P2_12_12_1$. Fig. 2 shows the molecular structure of (IIo) and the atomic labelling scheme. Selected bond lengths and angles are listed in Table 3.

Because of the unusual crystallization behaviour, the crystallization experiments were repeated and were shown to be reproducible. Furthermore, mixtures of (IIm) and (IIo) are obtained by crystallization at 278 K. One dimorph can be transformed into the other by complete dissolution of the crystals in *n*-hexane and 1,2-dimethoxyethane, followed by selection of the crystallization conditions. Analysis of (IIo) with differential thermal analysis and thermogravimetry (DTA/TG) shows that there is a weakly endothermic effect at 349 K. Cooling of the sample to room temperature and repeated heating shows that this endothermic effect no longer occurs. This hints at a transformation point at 349 K from the orthorhombic to the monoclinic form. The DTA sample melts
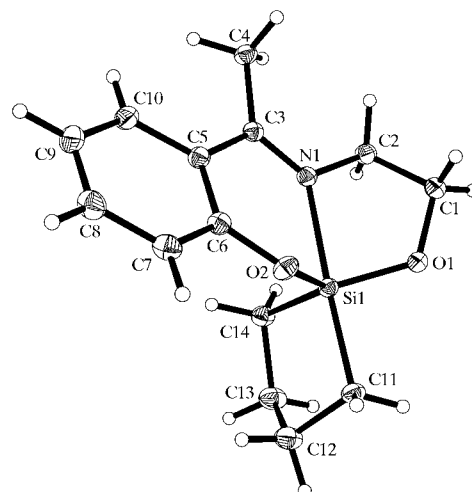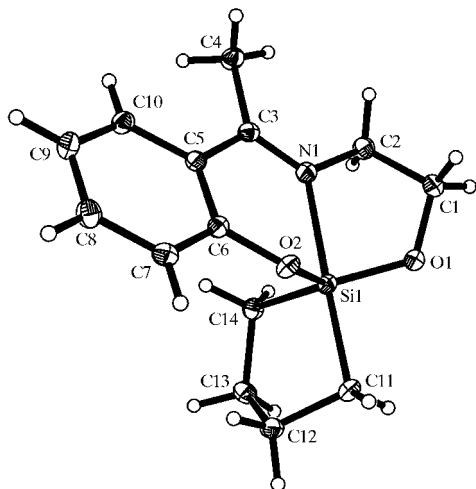

Figure 1
The molecular structure of form (IIm), drawn with 50% probability displacement ellipsoids. (Atom coordinates were inverted to facilitate comparison of the two forms.)

after repeated heating at 387 K. Investigation of a sample of (IIo) with powder diffraction shows the presence of orthorhombic and monoclinic phases in the finely ground substance. Therefore, we assume that the sample of (IIo) is contaminated by small amounts of (IIm). Heating of this sample to 363 K shows that a complete transformation into the monoclinic phase takes place. It seems, therefore, that (IIm) is the thermodynamically stable modification and (IIo) is a kinetically formed modification. Usually the thermodynamically more stable product has the greater density (Bernstein, 2003). Exceptions to this rule have been discussed in the literature (Burger & Ramberger, 1979). In the present case, the less stable orthorhombic form has the greater density.

The two molecular structures have common features. The Si atom is bound to the cyclopentane ring and to atoms O1, N1 and O2 of the chelate ligand. The coordination geometry is trigonal bipyramidal, as seen from the bond angles. Atoms N1 and C11 occupy the apical positions, with a C11—Si1—N1 angle of 177.51 (5)° for (IIm) and 178.35 (6)° for (IIo); atoms O1, O2 and C14 are situated in the equatorial plane. The chelate ligand coordinates in a capping fashion, with the two terminal O atoms in equatorial positions and the central N atom in an apical position. The Si—O bonds are rather short, at 1.676 (1)–1.712 (1) Å. The coordinative bond Si1—N1 is substantially longer [2.067 (1) and 2.055 (1) Å]. The Si—O bond to phenolate atom O2 is somewhat longer than that to aliphatic atom O1. This can be explained by postulating a stronger C—O bond from the phenoxy group and was also observed in related silicon and titanium complexes (Böhme & Günther, 2006, 2007). The Si1—C11 bond is longer than Si1—C14, consistent with the different positions of these two C atoms in the coordination polyhedron. The main differences between the molecular structures are found in the bond angles in the equatorial plane. Form (IIm) has O1—Si1—O2 and O1—Si1—C14 angles of *ca* 121°, and an O2—Si1—C14 angle of 115.72 (5)°. In (IIo), the first two angles are expanded to *ca* 123°, and the latter is compressed to only 111.44 (6)°. These
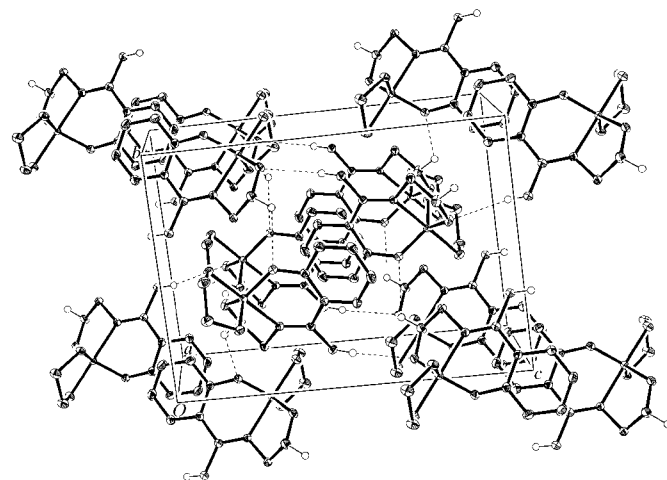
differences are illustrated by a least-squares fit of the two molecules (Fig. 3). The fit of atoms Si1, O1, O2, N1 and C1–C11 has an r.m.s. deviation of 0.0921 Å. The plot clearly shows the differing orientations of the five-membered ring.

Furthermore, the two structures are different with respect to the conformation of the silacyclopentane ring. The plane of the envelope is formed by atoms C11, Si1, C14 and C13 [the r.m.s. deviation of fitted atoms is 0.026 Å for (IIo) and 0.053 Å for (IIm)]. Atom C12 lies out of this plane by 0.669 (2) Å in (IIo) and 0.609 (2) Å in (IIm). This means that the envelope of the silacyclopentane ring is more folded in (IIo).
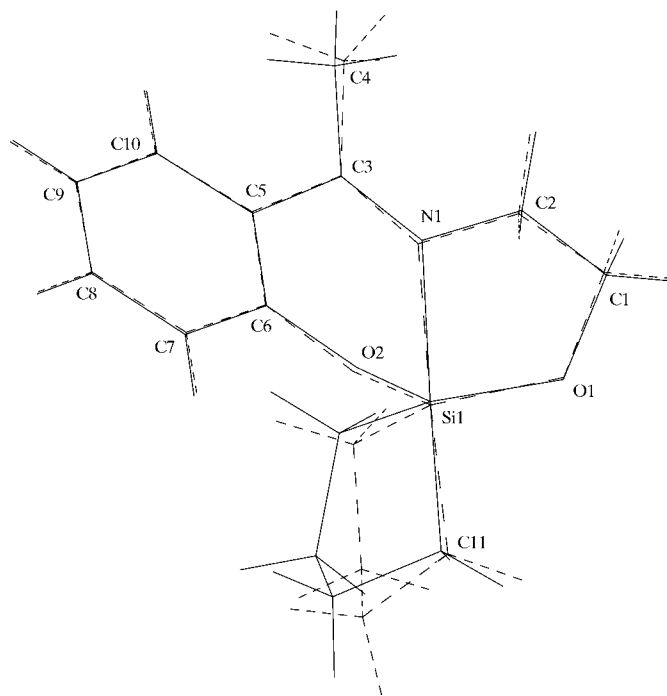
Figure 3
A least-squares fit of the two structures. The solid line indicates form (IIo) and the broken line form (IIm). Fitted atoms are labelled.

Figure 2
The molecular structure of form (IIo), drawn with 50% probability displacement ellipsoids.

Figure 4
The packing of (IIm), showing the stacking of the molecules parallel to the *a* axis and hydrogen bonds as dashed lines. Displacement ellipsoids are drawn at the 50% probability level. H atoms that do not participate in hydrogen bonding have been omitted for clarity.
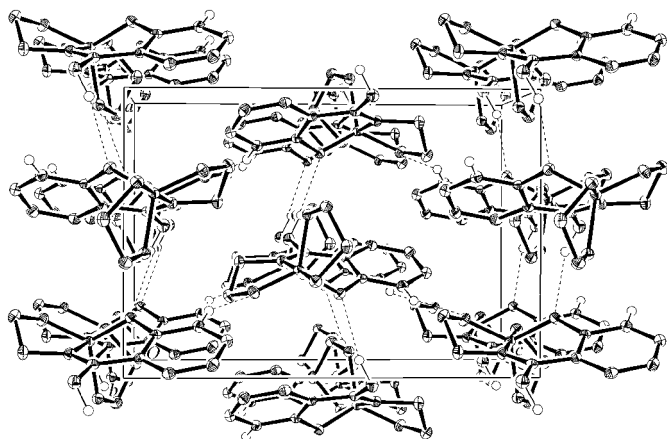
Figure 5
The packing of (IIo), viewed parallel to the b axis, showing hydrogen bonds as dashed lines. Displacement ellipsoids are drawn at the 50% probability level. H atoms that do not participate in hydrogen bonding have been omitted for clarity.

The polymorphs necessarily show major differences in molecular packing; whereas form (IIm) is a racemate, only one enantiomer is present in the packing structure of (IIo). The main characteristic of the (IIm) packing is the stacking of the substituted benzene rings (Fig. 4). These rings form pairs with a distance of 3.430 Å (normal between least-squares planes; symmetry code: $-x + 1$, $-y + 1$, $-z + 1$). The distance between successive pairs is 4.076 Å (normal between least-squares planes; symmetry code: $-x + 2$, $-y + 1$, $-z + 1$). Besides these contacts there are also two weak intermolecular interactions (see Table 2). The packing of form (IIo) (Fig. 5) shows two weak intermolecular interactions, one of which, C7—H7···O1($-x + \frac{3}{2}$, $-y + 1$, $z - \frac{1}{2}$), is essentially linear (Table 4).

Experimental

2-[1-(2-Hydroxyethylimino)ethyl]phenol, (I), was prepared by the reaction of *o*-hydroxyacetophenone (10.89 g, 0.08 mol) with 2-amino-ethanol (4.76 g, 0.078 mol) in absolute ethanol (150 ml). The mixture was refluxed for 2 h, cooled to room temperature and the volume of the solvent reduced on a rotary evaporator to about 50 ml. The remaining solid was filtered off, washed twice with small portions of diethyl ether and dried in air overnight [yellow crystals, yield 14.44 g (100%), m.p. 366 K]. The preparation of (II) was performed in Schlenk tubes under argon with dry and air-free solvents. Compound (II) was prepared by reaction of triethylamine (5.1 ml, 3.72 g, 36.8 mmol) and 1,1-dichlorosilacyclopentane (2.59 g, 16.7 mmol) with (I) (3.0 g, 16.7 mmol) in dry tetrahydrofuran at 273 K. A white precipitate of triethylamine hydrochloride formed immediately upon addition of (I). The reaction mixture was warmed to room temperature and stirred for one week. The triethylamine hydro-chloride was filtered off and washed with tetrahydrofuran. The solvent was removed *in vacuo* from the resulting clear yellow solu-tion. The remaining solid was extracted with *n*-hexane and a small amount of 1,2-dimethoxyethane. Filtration of this solution gave the solid product for NMR investigations and a suitable solution for growing single crystals. Analysis calculated for $C_{14}H_{19}NO_2Si$: C 64.33, H 7.33, N 5.36%; found: C 64.57, H 7.26, N 5.54%. ^{1}H NMR (CDCl$_3$): δ 0.26–0.33 (m, 4H, CH$_2$—Si), 1.32–1.42 (m, 4H, CH$_2$), 2.41 (s, 3H,

CH$_3$), 3.79–3.89 (m, 4H, CH$_2$—N, CH$_2$—O), 6.97–7.03 (m, 2H, ar), 7.37–7.55 (m, 2H, ar). ^{13}C NMR (CDCl$_3$): δ 14.02 (CH$_2$—Si), 17.11 (CH$_3$), 25.28 (CH$_2$), 48.28 (CH$_2$—N), 59.20 (CH$_2$—O), 119.97, 121.91, 122.46, 127.98, 133.72 (ar), 158.57 (C=N), 165.76 (ar, C—O). ^{29}Si NMR (CDCl$_3$): δ −52.99.

Form (IIm)

Crystal data

$C_{14}H_{19}NO_2Si$	$V = 1321.8\ (5)$ Å^3
$M_r = 261.39$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 8.2780\ (17)$ Å	$\mu = 0.17$ mm^{-1}
$b = 10.694\ (2)$ Å	$T = 93\ (2)$ K
$c = 15.155\ (3)$ Å	$0.60 \times 0.40 \times 0.33$ mm
$\beta = 99.86\ (3)°$	

Data collection

Bruker SMART CCD area-detector diffractometer	25940 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	3522 independent reflections
$T_{min} = 0.90$, $T_{max} = 0.95$	3115 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$	164 parameters
$wR(F^2) = 0.102$	H-atom parameters constrained
$S = 1.07$	$\Delta\rho_{max} = 0.83$ e Å^{-3}
3522 reflections	$\Delta\rho_{min} = -0.32$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for form (IIm).

Si1—O1	1.687 (1)	Si1—C11	1.929 (1)
Si1—O2	1.706 (1)	Si1—N1	2.067 (1)
Si1—C14	1.907 (1)		
O1—Si1—O2	121.37 (5)	C14—Si1—C11	92.21 (6)
O1—Si1—C14	121.40 (5)	O1—Si1—N1	82.58 (4)
O2—Si1—C14	115.72 (5)	O2—Si1—N1	85.40 (5)
O1—Si1—C11	95.26 (5)	C14—Si1—N1	89.98 (5)
O2—Si1—C11	94.71 (5)	C11—Si1—N1	177.51 (5)

Table 2
Short intermolecular contacts (Å, °) in form (IIm).

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4B···O1^{i}	0.98	2.59	3.445 (2)	147
C1—H1B···O2^{ii}	0.99	2.68	3.330 (2)	124

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

Form (IIo)

Crystal data

$C_{14}H_{19}NO_2Si$	$V = 1310.53\ (10)$ Å^3
$M_r = 261.39$	$Z = 4$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 9.5798\ (4)$ Å	$\mu = 0.17$ mm^{-1}
$b = 9.9284\ (5)$ Å	$T = 93\ (2)$ K
$c = 13.7788\ (6)$ Å	$0.56 \times 0.50 \times 0.35$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	15312 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	3813 independent reflections
$T_{min} = 0.90$, $T_{max} = 0.95$	3525 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.034$

organic compounds

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$	$\Delta\rho_{max} = 0.49$ e Å^{-3}
$wR(F^2) = 0.087$	$\Delta\rho_{min} = -0.23$ e Å^{-3}
$S = 1.04$	Absolute structure: Flack (1983),
3813 reflections	1638 Friedel pairs
164 parameters	Flack parameter: -0.10 (9)
H-atom parameters constrained	

Table 3
Selected geometric parameters (Å, °) for form (IIo).

Si1—O1	1.676 (1)	Si1—C11	1.913 (1)
Si1—O2	1.712 (1)	Si1—N1	2.055 (1)
Si1—C14	1.895 (2)		
O1—Si1—O2	123.32 (6)	C14—Si1—C11	92.14 (6)
O1—Si1—C14	123.55 (6)	O1—Si1—N1	82.55 (5)
O2—Si1—C14	111.44 (6)	O2—Si1—N1	85.44 (5)
O1—Si1—C11	96.29 (6)	C14—Si1—N1	89.49 (5)
O2—Si1—C11	94.23 (6)	C11—Si1—N1	178.35 (6)

Table 4
Short intermolecular contacts (Å, °) in form (IIo).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C7—H7$\cdots$O1^i	0.95	2.52	3.424 (2)	159
C4—H4$C\cdots$O2^{ii}	0.98	2.69	3.406 (2)	130

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

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

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