

Formation of a silicon-containing macrocycle with a pyridoxalimine Schiff base ligand

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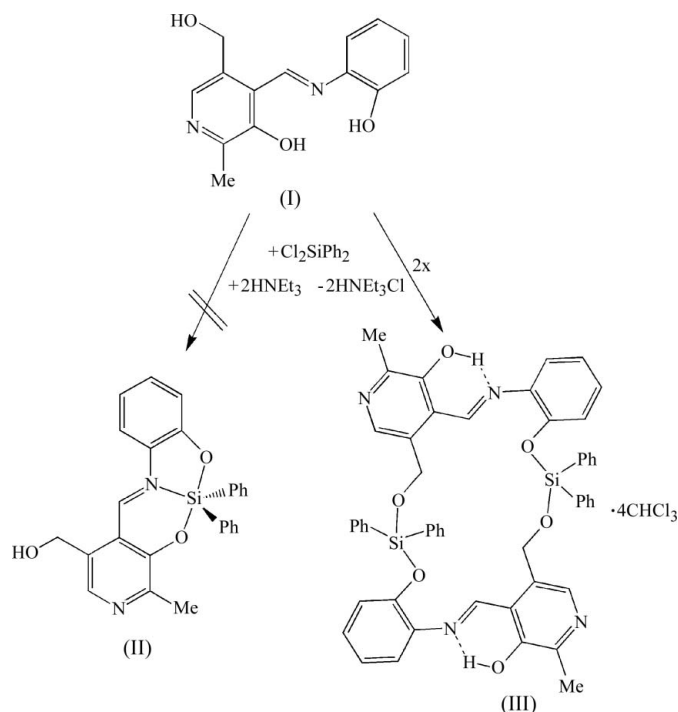
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The reaction of dichlorodiphenylsilane with a polydentate Schiff base ligand derived from pyridoxal and 2-hydroxyaniline yields the macrocyclic centrosymmetric silicon compound 9,27-dimethyl-3,3,21,21-tetraphenyl-2,4,20,22-tetraoxa-8,13,26,31-tetraaza-3,21-disilapentacyclo[30.4.0.0^{6,11}.0^{14,19}.0^{24,29}]-hexatrieca-1(32),6,8,10,12,14,16,18,24,26,28,30,33,35-tetradecane-10,28-diol chloroform tetrasolvate, C₅₂H₄₄N₄O₆Si₂·4CHCl₃. The asymmetric unit contains half of the macrocycle and two molecules of chloroform, with C—H···O and C—H···N contacts binding the two guests to the host in the crystal structure. This macrocyclic silicon compound represents a promising host for molecular-recognition processes and for the construction of nanostructures.

Comment

Carbon-based macrocycles are used frequently as hosts for molecular-recognition processes (Weber & Vögtle, 1996). The macrocycle provides the necessary preorganization of the host for the inclusion process (König, Rödel, Bubenitschek, Jones & Thondorf, 1995). The incorporation of other main group elements into the macrocycles gives these compounds new binding properties (König, Rödel, Bubenitschek & Jones, 1995). Earlier work has shown the coordinative ability of silicon (Jung & Xia, 1988), phosphorous (Caminade & Majoral, 1994) and tin (Blanda *et al.*, 1989) as bridging atoms in macrocycles. During our work on silicon complexes with *O,N,O'*-tridentate ligands of Schiff base type, we used pyridoxal as a component of the ligand system. The reaction of pyridoxal hydrochloride with *o*-aminophenol in the presence of sodium methanolate gives the polydentate ligand 5-hydroxymethyl-4-[(2-hydroxyphenyl)iminomethyl]-2-methylpyridin-3-ol, (I) (see scheme). There are numerous potential docking sites in the ligand molecule: the pyridine N atom, one aliphatic and two phenolic hydroxyl groups, and the imino N atom. The presence of diverse functional groups in (I) makes it difficult to predict the molecular structure of the reaction

product with halogenosilanes. It was our initial goal to prepare a pentacoordinate silicon complex like (II). Surprisingly, the macrocyclic silicon compound (III) was obtained from the reaction of (I) with Ph₂SiCl₂ in tetrahydrofuran in the presence of NEt₃ as a supporting base to remove the hydrogen chloride which is formed during the reaction. The first hint of the formation of a tetracoordinate silicon complex was found in the ²⁹Si NMR spectrum: compound (III) has a single resonance signal at −32.8 p.p.m. The ¹H and ¹³C NMR spectra did not give further information apart from the presence of the ligand system including one hydroxyl group.



Crystallization of (III) from a chloroform solution over a period of several weeks at 278 K yielded single crystals of the title chloroform solvate, (III), which crystallizes in the triclinic space group *P* $\bar{1}$ with half of the macrocycle and two chloroform molecules in the asymmetric unit (Fig. 1). The macrocycle is thus generated by a crystallographic inversion centre (Fig. 2). The Si atom is bound to two phenyl groups, to phenol atom O3 and to the aliphatic O atom from the next ligand molecule, thus forming a macrocycle (Fig. 2). The Si—O bonds are short (Table 1), but in the range for comparable Si—O bonds (Wagler *et al.*, 2005; Böhme *et al.*, 2006; Böhme & Günther, 2007; Böhme & Foehn, 2007). The coordination geometry around the Si atom is distorted tetrahedral, with bond angles between 104.9 (1) and 117.1 (1)° (Table 1). The O₂Si(Ph)₂ group is a common structural motif. Some macrocycles with a similar distorted tetrahedral coordination environment at the Si atom have been described previously (Cragg *et al.*, 1991; Rezzonico *et al.*, 1998; Gómez & Farfán, 1999). The rather large bond angles at oxygen (Table 1) are explained by the ionic character of the Si—O bonds (Gillespie & Johnson, 1997).

Two planes can be used to characterize the conformation of the dianion of the ligand molecule, (II). In the corresponding

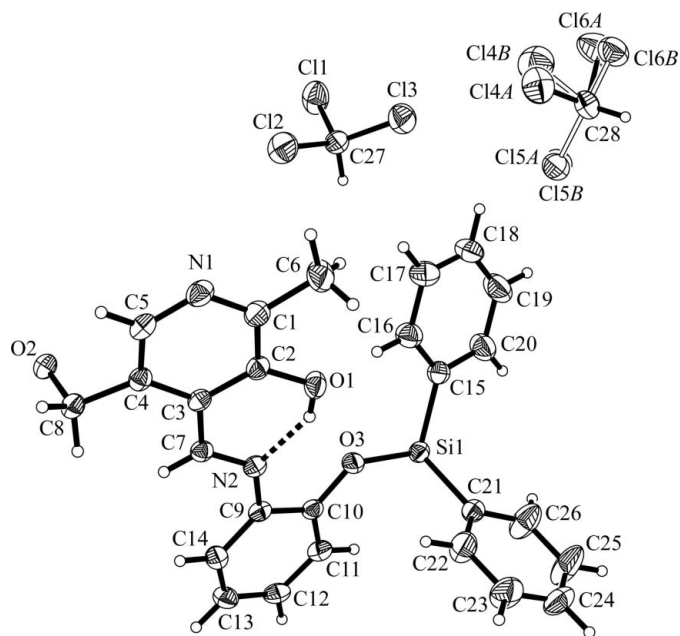


Figure 1

The asymmetric unit of (III), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The dashed line indicates the intramolecular hydrogen bond.

fragment of the molecule of (III), the plane of the C9–C14 benzene ring makes an angle of $17.5(2)^\circ$ with the plane of the pyridine ring (C1–C5/N1). Nearly planar with this latter ring is the six-membered pseudo-ring (Fig. 1) consisting of atoms H1/O1/C2/C3/C7/N2 [at an angle of $2.1(1)^\circ$ to the pyridine ring]. The planarity of the six-membered pseudo-ring is caused by a strong intramolecular O–H...N interaction (entry 1, Table 2). The formation of hydrogen bonds between the imine N atom and an *ortho* hydroxyl group is a feature which is often observed in Schiff bases with *o*-hydroxy groups (Hökelek *et al.*, 2004; Filarowski *et al.*, 1999).

Two independent chloroform solvent molecules are incorporated into the crystal structure. Contacts with the disordered Cl atoms of the C28-based solvate (Fig. 1) are not considered important for crystal structure formation. The nondisordered solvate shows only one very weak chlorine contact (C22–H22...Cl1 = 2.90 \AA and 144°) but is bound to the guest *via* a C28–H28...O1 intermolecular contact (entry 3, Table 2). The other guest is connected to the host *via* a C–H...N contact (Fig. 3; entry 2, Table 2). One C8–H8A... π contact between one of the aliphatic H atoms, H8A, and the pyridine unit is localized with a hydrogen-to-centre distance of 2.94 \AA and a C8–H8A...Cg angle of 109° , where Cg is the centre of the C1–C5/N1 ring at the symmetry position $(2 - x, 1 - y, -z)$. This contact forms intermolecular chains of the host molecule along the crystallographic *a* axis (not shown in Fig. 3). These intermolecular contacts of weak to moderate strength in the crystal structure of (III) indicate potential coordination sites for interactions with other guest molecules.

Numerous potential bonding sites in the ligand system, along with the cavity of the macrocycle, provide promise for

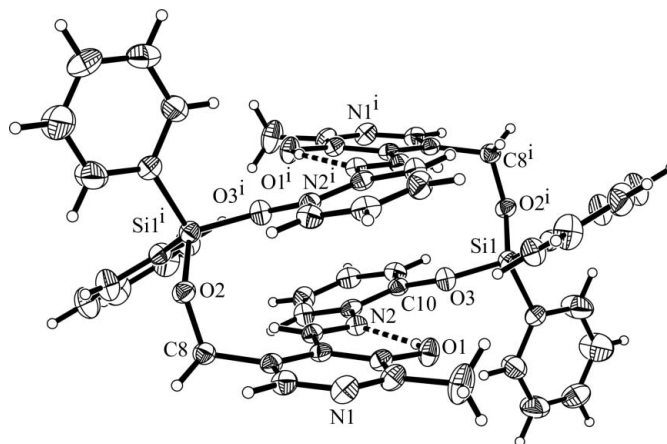


Figure 2

The molecular structure of (III). Displacement ellipsoids are drawn at the 50% probability level. The dashed line indicates the intramolecular hydrogen bond. Chloroform solvent molecules have been omitted. [Symmetry code: (i) $-x + 1, -y + 1, -z$.]

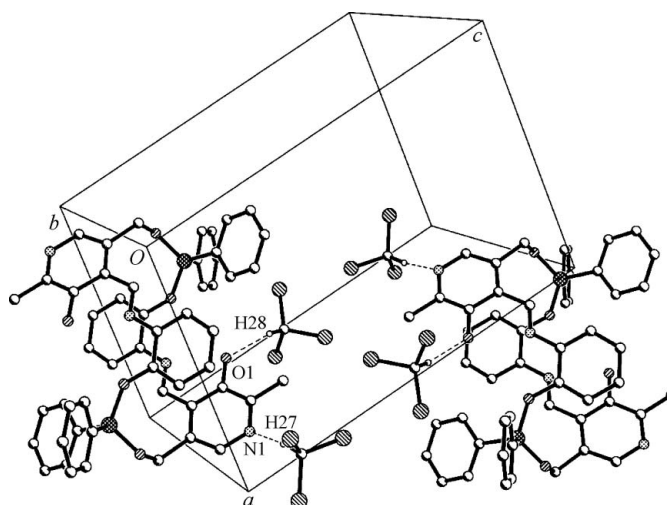


Figure 3

A partial packing diagram for (III), showing key intermolecular interactions. H atoms not involved in the hydrogen bonds have been omitted for clarity.

(III) as a host molecule in supramolecular recognition processes. Furthermore, the available OH, azomethine N and pyridine N groups could be useful for the construction of nanostructures *via* complexation with transition metals (Leininger *et al.*, 2000).

Experimental

5-Hydroxymethyl-4-[(2-hydroxyphenyl)iminomethyl]-2-methylpyridin-3-ol, (I), was prepared as follows. To pyridoxal hydrochloride (4.06 g, 20 mmol) dissolved in methanol was added a solution of sodium methanolate (1.08 g, 20 mmol) in methanol. A solution of *o*-aminophenol (2.18 g, 20 mmol) in methanol was added dropwise. The suspension was boiled at reflux temperature. The colour of the solution became orange and a precipitate was formed. After 2 h, the suspension was cooled to room temperature and the precipitate was filtered off. The solid was washed with small amounts of water to remove sodium chloride, followed by diethyl ether. Compound (I)

was obtained as an orange solid (yield 4.13 g, 80%; m.p. 495 K). The preparation of (III) was performed in Schlenk tubes under argon with dry and air-free solvents. Compound (III) was prepared by the reaction of triethylamine (1.7 ml, 1.21 g, 12.0 mmol) and dichlorodiphenylsilane (1.22 g, 4.8 mmol) with (I) (1.25 g, 4.8 mmol) in dry tetrahydrofuran at room temperature. A white precipitate of triethylamine hydrochloride formed upon stirring the mixture for 6 d. After this period, the triethylamine hydrochloride was filtered off and washed with tetrahydrofuran. The solvent was removed *in vacuo* from the resulting clear red solution. The remaining solid was extracted with 1,2-dimethoxyethane. Addition of hexane, cooling to 278 K and filtration of this sample gave a red solid product (yield 1.48 g, 70.3%; m.p. 485 K). Single crystals of the title compound, (III), were obtained by recrystallization from CHCl_3 . NMR data are available in the archived CIF.

Crystal data

$\text{C}_{52}\text{H}_{44}\text{N}_4\text{O}_6\text{Si}_2 \cdot 4\text{CHCl}_3$	$\gamma = 98.733 (1)^\circ$
$M_r = 1354.56$	$V = 1525.91 (8) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 1$
$a = 9.8831 (3) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 11.2094 (3) \text{ \AA}$	$\mu = 0.64 \text{ mm}^{-1}$
$c = 14.7584 (4) \text{ \AA}$	$T = 153 (2) \text{ K}$
$\alpha = 102.853 (2)^\circ$	$0.33 \times 0.30 \times 0.22 \text{ mm}$
$\beta = 101.899 (1)^\circ$	

Data collection

Bruker SMART CCD area-detector diffractometer	14146 measured reflections
Absorption correction: multi-scan (<i>SADABS</i> ; Sheldrick, 1996)	6493 independent reflections
$T_{\min} = 0.818$, $T_{\max} = 0.873$	5116 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.019$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$	126 restraints
$wR(F^2) = 0.114$	H-atom parameters constrained
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.62 \text{ e \AA}^{-3}$
6493 reflections	$\Delta\rho_{\text{min}} = -0.44 \text{ e \AA}^{-3}$
391 parameters	

Table 1

Selected geometric parameters (\AA , $^\circ$).

Si1—O2 ⁱ	1.6310 (19)	Si1—C21	1.852 (3)
Si1—O3	1.6591 (19)	Si1—C15	1.859 (3)
O2 ⁱ —Si1—O3	113.09 (10)	O3—Si1—C15	104.87 (11)
O2 ⁱ —Si1—C21	105.25 (11)	C21—Si1—C15	117.06 (12)
O3—Si1—C21	109.07 (11)	C8—O2—Si1 ⁱ	126.29 (16)
O2 ⁱ —Si1—C15	107.75 (11)	C10—O3—Si1	129.71 (16)

Symmetry code: (i) $-x + 1, -y + 1, -z$.

The final automatic data collection scan could not be completed due to loss of the crystal from the beam, with a subsequent gap in the inner-shell data. One of the two symmetry-independent chloroform molecules is disordered over two orientations. The site-occupation factors were refined and gave a final value of 0.739 (11) for the major orientation (Cl4A–Cl6A). Rigid bond restraints were applied to the U_{ij} values of one phenyl ring (C24–C26) and to the disordered chloroform molecule at C28 [12 restraints with the DELU command in *SHELXL97* (Sheldrick, 2008)]. Further restraints were used to generate similar U_{ij} values and to restrain the atoms to be approximately isotropic for the atoms of one phenyl ring and for both

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 \cdots N2	0.84	1.77	2.511 (3)	147
C27—H27 \cdots N1	1.00	2.16	3.149 (4)	168
C28—H28 \cdots O1	1.00	2.35	3.295 (4)	158

chloroform molecules (30 restraints with the SIMU command and 84 restraints with the ISOR command in *SHELXL97*). All C-bound H atoms were positioned geometrically, with C—H = 0.95, 0.98, 0.99 or 1.00 \AA for aryl, CH_3 , CH_2 or tertiary C—H groups, respectively, and refined in riding mode, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl or $1.2U_{\text{eq}}(\text{C})$ for all other H atoms. The H atom bonded to atom O1 was positioned geometrically, with O—H = 0.84 \AA , and refined in riding mode, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

Data collection: *SMART* (Bruker, 2004); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *XP* in *SHELXTL-Plus* (Release 4.1; Sheldrick, 2008); 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: GA3110). Services for accessing these data are described at the back of the journal.

References

- Blanda, M. T., Horner, J. H. & Newcomb, M. (1989). *J. Org. Chem.* **54**, 4626–4636.
- Böhme, U. & Foehn, I. C. (2007). *Acta Cryst.* **C63**, o613–o616.
- Böhme, U. & Günther, B. (2007). *Inorg. Chem. Commun.* **10**, 482–484.
- Böhme, U., Wiesner, S. & Günther, B. (2006). *Inorg. Chem. Commun.* **9**, 806–809.
- Bruker (2004). *SMART* (Version 5.628) and *SAINT* (Version 6.45a). Bruker AXS Inc., Madison, Wisconsin, USA.
- Caminade, A.-M. & Majoral, J. P. (1994). *Chem. Rev.* **94**, 1183–1213.
- Cragg, R. H., Jeffery, J. C. & Went, M. J. (1991). *J. Chem. Soc. Dalton Trans.* pp. 137–142.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Filarowski, A., Głowiaka, T. & Koll, A. (1999). *J. Mol. Struct.* **484**, 75–89.
- Gillespie, R. J. & Johnson, S. A. (1997). *Inorg. Chem.* **36**, 3031–3039.
- Gómez, E. & Farfán, N. (1999). *Heteroatom Chem.* **10**, 351–354.
- Hökelek, T., Bilge, S., Demiriz, Ş., Özgüç, B. & Kılıç, Z. (2004). *Acta Cryst.* **C60**, o803–o805.
- Jung, M. E. & Xia, H. (1988). *Tetrahedron Lett.* **29**, 297–300.
- König, B., Rödel, M., Bubenitschek, P. & Jones, P. G. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 661–662.
- König, B., Rödel, M., Bubenitschek, P., Jones, P. G. & Thondorf, I. (1995). *J. Org. Chem.* **60**, 7406–7410.
- Leininger, S., Olenyuk, B. & Stang, P. J. (2000). *Chem. Rev.* **100**, 853–908.
- Rezzonico, B., Grignon-Dubois, M., Laguerre, M. & Leger, J.-M. (1998). *Organometallics*, **17**, 2656–2664.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Wagler, J., Böhme, U., Brendler, E., Thomas, B., Goutal, S., Mayr, H., Kempf, B., Remennikov, G. Y. & Roewer, G. (2005). *Inorg. Chim. Acta*, **358**, 4270–4286.
- Weber, E. & Vögtle, F. (1996). *Comprehensive Supramolecular Chemistry*, Vol. 2, edited by J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle & J.-M. Lehn, pp. 1–28. Oxford: Pergamon Press.