# Formation of a macrocycle from dichlorodimethyl-silane and a pyridoxalimine Schiff base ligand

Uwe Böhme,[a]* Anke Schwarzer[b] and Betty Günther[a]

[a]Institut für Anorganische Chemie, Technische Universität Bergakademie Freiberg, Leipziger Str. 29, 09599 Freiberg, Germany, and [b]Institut für Organische Chemie, Technische Universität Bergakademie Freiberg, Leipziger Str. 29, 09599 Freiberg, Germany. *Correspondence e-mail: uwe.boehme@chemie.tu-freiberg.de

The reaction of dichlorodimethylsilane with a polydentate Schiff base ligand derived from pyridoxal and 2-ethanolamine yielded the macrocyclic silicon compound (8$E$,22$E$)-4,4,12,18,18,26-hexamethyl-3,5,17,19-tetraoxa-8,13,22,27-tetraaza-4,18-disil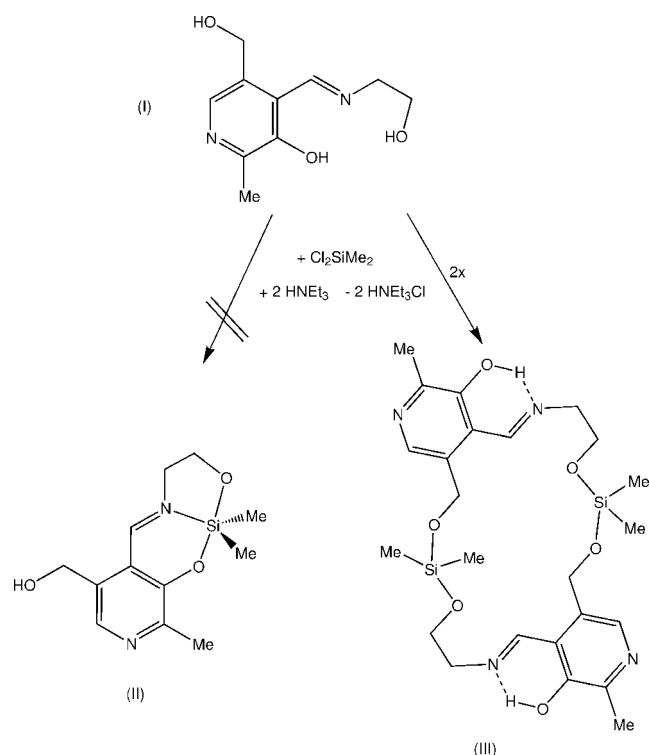atricyclo[22.4.0.0$^{10,15}$]octacosa-1(24),8,10,12,14,22,25,27-octa-ene-11,25-diol, $C_{24}H_{36}N_4O_6Si_2$. The asymmetric unit contains the half macrocycle with an intramolecular O—H···N hydrogen bond between the imine nitrogen atom and a neighbouring oxygen atom. The crystal structure is dominated by C—H···O and C—H···$\pi$ interactions, which form a high ordered molecular network.

## 1. Chemical context

The heterocyclic aldehyde pyridoxal is one of the active forms of vitamin $B_6$. This vitamin is an essential cofactor to a large number of enzymes that catalyze many reactions of amino acids (Sykes *et al.*, 1991). The coordination chemistry of Schiff bases generated from amino acids and pyridoxal with transition metal ions has been investigated intensive (Christensen, 1957; Long *et al.*, 1980; Dawes *et al.*, 1982; Walz *et al.*, 1983; Rao *et al.*, 1985; Astheimer *et al.*, 1985; Sykes *et al.*, 1991; Costa Pessoa *et al.*, 1999). We are working on silicon complexes with tridentate *O,N,O*-ligands (Böhme & Günther, 2007*a*; Böhme *et al.*, 2006; Paul *et al.*, 2014; Warncke *et al.*, 2012; Schwarzer *et al.*, 2018). Therefore, we prepared a Schiff base from pyridoxal and 2-aminoethanol as a potential *O,N,O*-ligand. The crystal structure of this molecule, 4-[(2-hydroxyethyl)iminomethyl]-5-hydroxymethyl-2-methylpyridine-3-ol (I), was published earlier (Böhme & Günther, 2007*b*). Compound (I) was used recently as ligand molecule to coordinate copper and silver ions (Annaraj & Neelakantan, 2014, 2015). Herein we report the results of reaction between (I) and dichlorodimethylsilane.

There are several potential coordination sites at the ligand molecule (I): the pyridine and the imino nitrogen atoms, two aliphatic and one phenolic hydroxyl groups. The presence of these functional groups makes it difficult to predict the structure of the reaction product with dichlorodimethylsilane. 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 $Me_2SiCl_2$. The reaction was performed in tetrahydrofuran in presence of triethylamine as supporting base to remove the hydrogen chloride, which is formed during the reaction. Recrystallization of the raw product from 1,2-dimethoxy-ethane and diethyl ether gave yellow crystals suitable for structure analysis.

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

| | | | |
|---|---|---|---|
| Si1—O2 | 1.6435 (9) | Si1—C12 | 1.8443 (14) |
| Si1—O3[i] | 1.6487 (9) | Si1—C11 | 1.8589 (15) |
| | | | |
| O2—Si1—O3[i] | 103.40 (5) | O3[i]—Si1—C11 | 109.52 (6) |
| O2—Si1—C12 | 106.94 (6) | C12—Si1—C11 | 113.16 (7) |
| O3[i]—Si1—C12 | 112.06 (6) | C8—O2—Si1 | 123.61 (8) |
| O2—Si1—C11 | 111.33 (7) | C10—O3—Si1[i] | 123.50 (8) |

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

macrocycle is generated by a crystallographic $C2$ axis through the centre of the macrocycle (Fig. 2). The silicon atom is bound to the two methyl groups and to the aliphatic oxygen atoms O2 and O3, thus forming a macrocycle (Fig. 2). A quite similar macrocycle has been obtained from the reaction of a related pyridoxal-derived Schiff base and dichlorodiphenyl-silane (Böhme *et al.*, 2008). The short Si—O bonds (see Table 1) are in the range for comparable Si—O bonds (Wagler *et al.*, 2005; Böhme *et al.*, 2006, 2008; Böhme & Günther, 2007a; Böhme & Foehn, 2007). The silicon atom is distorted tetra-hedral with bond angles between 103.40 (5) and 113.16 (7)° (Table 1). The rather large bond angles at the oxygen atoms (see Table 1) have been explained by the ionic character of the Si—O bonds (Gillespie & Johnson, 1997). There is a strong intramolecular O—H⋯N interaction (entry 1, Table 2) between the imine nitrogen atom N2 and the O1—H1 group in the neighbouring position at the pyridoxal ring. The formation of hydrogen bridges between the imine nitrogen atom and an *ortho*-hydroxyl group is a feature that is often observed in Schiff bases with *o*-hydroxy groups (Hökelek *et al.*, 2004; Filarowski *et al.*, 1999). This strong intramolecular O—H⋯N interaction leads to a six-membered pseudo ring consisting of H1—O1—C2—C3—C7—N2. This pseudo ring is planar with an r.m.s. deviation of 0.009 Å from the ring plane. According to the graph-set notation proposed by Etter *et al.* (1990), these

## 2. Structural commentary

Compound (III) crystallizes in the monoclinic space group $I2/c$ with the half macrocycle in the asymmetric unit. Fig. 1 shows the asymmetric unit and the atomic labelling scheme. The
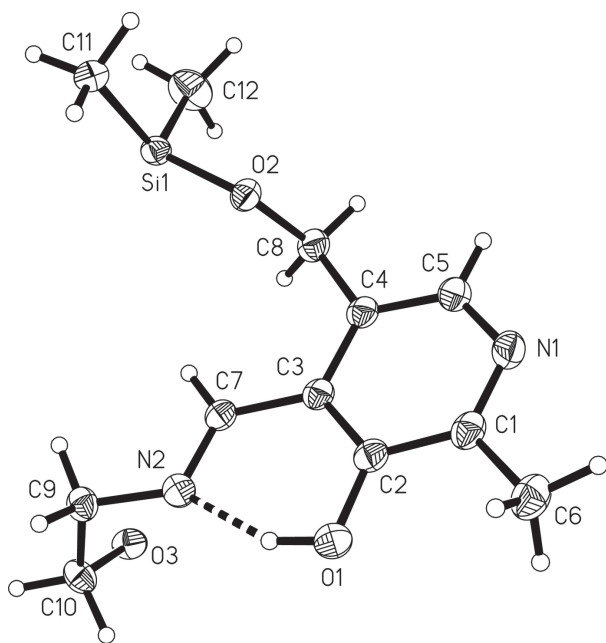


**Figure 1**
The asymmetric unit of (III), drawn with 50% probability displacement ellipsoids. The dashed line shows the intramolecular O1—H1⋯N2 hydrogen bond.
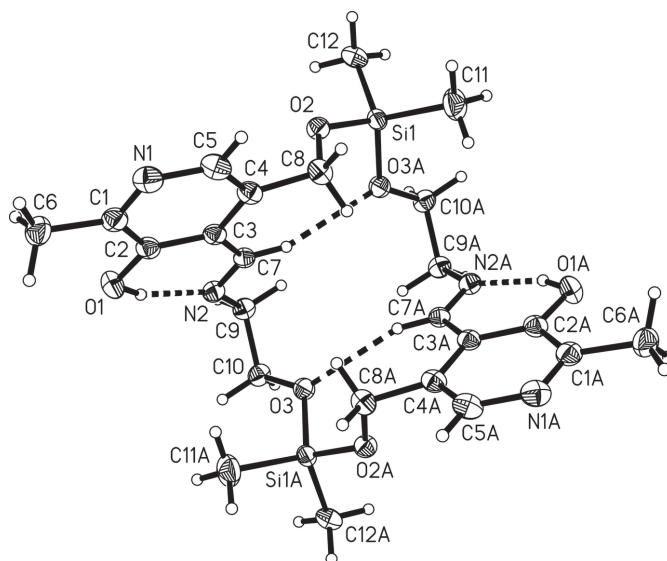


**Figure 2**
The molecular structure of (III), drawn with 50% probability displacement ellipsoids.

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

Cg1 is the centroid of the N1/C1–C5 ring.

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|---|---|---|---|---|
| $\text{O1}-\text{H1}\cdots\text{N2}$ | 0.90 (2) | 1.76 (2) | 2.5923 (15) | 153.2 (18) |
| $\text{C5}-\text{H5}\cdots\text{O1}^{\text{ii}}$ | 0.95 | 2.69 | 3.5451 (16) | 151 |
| $\text{C6}-\text{H6}A\cdots\text{O2}^{\text{iii}}$ | 0.98 | 2.59 | 3.3464 (17) | 134 |
| $\text{C7}-\text{H7}\cdots\text{O3}^{\text{i}}$ | 0.95 | 2.57 | 3.4882 (15) | 162 |
| $\text{C9}-\text{H9}B\cdots\text{O2}^{\text{iv}}$ | 0.99 | 2.60 | 3.5087 (16) | 153 |
| $\text{C9}-\text{H9}B\cdots Cg1^{\text{iv}}$ | 0.99 | 3.31 | 4.039 (2) | 131 |
| $\text{C11}-\text{H11}A\cdots Cg1^{\text{ii}}$ | 0.98 | 2.85 | 3.7880 (2) | 160 |

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

hydrogen bonds form motifs with an $S_1^1(6)$ graph-set descriptor. The hydrogen bonds C7—H7···O3 link different parts within one macrocycle via intra-annular hydrogen bonds (Fig. 2).

## 3. Supramolecular features

A bifurcated intermolecular C—H···O interaction is observed at O2 (Table 2). The interaction of C6—H6A···O2 and C5—H5···O1 results in a chain along the crystallographic b-axis. The C—H···O interaction of C9—H9B with O2 connects adjacent chains (Fig. 3).

Apart from the relevant C—H···O interaction, two C—H···$\pi$ contacts with the pyridine moiety (Cg1) are observed. First, a bifurcation at H9B (d = 3.31 Å) shows up within the C—H···O chains along the c axis. Furthermore, C11—H11A···Cg1 (d = 2.85 Å) supports the C—H···O interactions of H5 and H6A.

In summary, the crystal structure is dominated by C—H···O and C—H···$\pi$ interactions, forming a highly ordered molecular network.

The potential bonding sites in combination with the cavity of the macrocycle makes (III) a suitable candidate for supramolecular recognition processes. The available pyridine N, azomethine N, and OH groups could be useful for the generation of nanostructures via complexation with transition metals (Leininger et al., 2000).
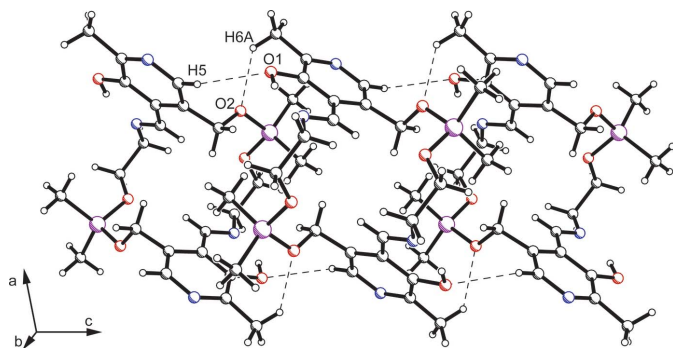


**Figure 3**
Packing excerpt of (III) showing C—H···O hydrogen bonds (dashed lines).

## 4. Database survey

A CSD search with ConQuest (Bruno et al., 2002) for macrocycles containing Schiff bases from pyridoxal and 2-aminoalcohols showed that only one comparable silicon compound exists (Böhme et al., 2008, refcode MOKVEO). The main differences between these two structures of silicon-containing macrocycles are as follows. First, (III) was found to crystallize without solvent while MOKVEO encloses chloro-fom molecules. Probably as a result, the symmetry is lower in MOKVEO (triclinic, $P\bar{1}$) than in (III) showing the monoclinic $I2/c$ symmetry. On the basis of the structure of (III) presented here and the former investigation (Böhme et al., 2008), it can be assumed that pyridoxalimine-derived Schiff bases prefer the formation of macrocycles with diorganosilane units. However, it seems to be possible that compound (I) can also act as a tridentate O,N,O-ligand, as was shown recently with a hexacoordinate titanium complex (Böhme & Günther, 2020).

## 5. Synthesis and crystallization

The preparation of (III) was performed in Schlenk tubes under argon with dry and air-free solvents.

Compound (III) was prepared by reaction of 4-[(2-hydroxyethyl)iminomethyl]-5-hydroxymethyl-2-methylpyridine-3-ol (I) (1.7 g, 8 mmol) with dichlorodimethylsilane (1.03 g, 8 mmol) in the presence of triethylamine (2.02 g, 20 mmol). The reaction was performed in dry tetrahydrofuran at room temperature. A white precipitate of triethylamine hydrochloride formed upon stirring of the mixture for five days. After this period, the triethylamine hydrochloride was filtered off and washed with tetrahydrofuran. The solvent was removed in vacuo from the resulting clear yellow solution. The remaining solid was extracted with 1,2-dimethoxyethane. Addition of diethyl ether and cooling to 278 K yielded yellow crystals of (III) (1.66 g, 78%, m.p. 390 K).

NMR (CDCl$_3$, 300 K, TMS, in p.p.m.): $^{29}$Si: −0.1. $^{1}$H: $\delta$ = 0.14 (s, Me$_2$Si, 6H), 2.50 (s, CH$_3$ pyridoxal, 3H), 3.71, 3.90 (t, N—CH$_2$—CH$_2$—O, 4H), 4.78 (s, CH$_2$—O pyridoxal, 2H), 7.89 (s, CH pyridoxal, 1H), 8.84 (s, HC=N, 1H), 14.05 (s, OH pyridoxal, 1H). $^{13}$C: 3.0 (Me$_2$Si), 22.0 (CH$_3$ pyridoxal), 63.3, 64.6 (N—CH$_2$—CH$_2$—O), 66.4 (CH$_2$—O pyridoxal), 122.6, 133.4, 140.8, 153.8, 157.8 (five C pyridoxal), 167.5 (HC=N).

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The hydrogen atom at O1 was refined freely. The methyl groups were refined as idealized rigid groups allowed to rotate but not tip (AFIX 137; C—H = 0.98 Å, H—C—H = 109.5°). Other hydrogens were included using a riding model starting from calculated positions (C—H$_{\text{aromatic}}$ = 0.95, C—H$_{\text{methylene}}$ = 0.99 Å). The $U_{\text{iso}}(\text{H})$ values were fixed at 1.5 (for the methyl H) or 1.2 times the equivalent $U_{\text{eq}}$ value of the parent carbon atoms.

# research communications

## References

Annaraj, B. & Neelakantan, M. A. (2014). *Anal. Methods* **6**, 9610–9615.

Annaraj, B. & Neelakantan, M. A. (2015). *Eur. J. Med. Chem.* **102**, 1–8.

Astheimer, H., Nepveu, F., Walz, L. & Haase, W. (1985). *J. Chem. Soc. Dalton Trans.* pp. 315–320.

Böhme, U. & Foehn, I. C. (2007). *Acta Cryst.* C**63**, o613–o616.

Böhme, U. & Günther, B. (2007*a*). *Inorg. Chem. Commun.* **10**, 482–484.

Böhme, U. & Günther, B. (2007*b*). *Acta Cryst.* C**63**, o641–o642.

Böhme, U. & Günther, B. (2020). *CSD Communication* (CCDC No. 2048270). CCDC, Cambridge, England. https://dx.doi.org/10.5517/ccdc.csd.cc26rd7m

Böhme, U., Günther, B. & Schwarzer, A. (2008). *Acta Cryst.* C**64**, o630–o632.

Böhme, U., Wiesner, S. & Günther, B. (2006). *Inorg. Chem. Commun.* **9**, 806–809.

Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* B**58**, 389–397.

Christensen, H. N. (1957). *J. Am. Chem. Soc.* **79**, 4073–4078.

Costa Pessoa, J., Cavaco, I., Correia, I., Duarte, M. T., Gillard, R. D., Henriques, R. T., Higes, F. J., Madeira, C. & Tomaz, I. (1999). *Inorg. Chim. Acta*, **293**, 1–11.

Dawes, H. M., Waters, J. M. & Waters, T. N. (1982). *Inorg. Chim. Acta*, **66**, 29–36.

Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* B**46**, 256–262.

Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.

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.

Hökelek, T., Bilge, S., Demiriz, Ş., Özgüç, B. & Kılıç, Z. (2004). *Acta Cryst.* C**60**, o803–o805.

Leininger, S., Olenyuk, B. & Stang, P. J. (2000). *Chem. Rev.* **100**, 853–908.

Long, G. J., Wrobleski, J. T., Thundathil, R. V., Sparlin, D. M. & Schlemper, E. O. (1980). *J. Am. Chem. Soc.* **102**, 6040–6046.

Paul, L. E. H., Foehn, I. C., Schwarzer, A., Brendler, E. & Böhme, U. (2014). *Inorg. Chim. Acta*, **423**, 268–280.

Rao, S. P. S., Manohar, H. & Bau, R. (1985). *J. Chem. Soc. Dalton Trans.* pp. 2051–2057.

Schwarzer, S., Böhme, U., Fels, S., Günther, B. & Brendler, E. (2018). *Inorg. Chim. Acta*, **483**, 136–147.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

Stoe (2009). *X-RED* and *X-AREA*. Stoe & Cie, Darmstadt, Germany.

Sykes, A. G., Larsen, R. D., Fischer, J. R. & Abbott, E. H. (1991). *Inorg. Chem.* **30**, 2911–2916.

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.

Walz, L., Paulus, H., Haase, W., Langhof, H. & Nepveu, F. (1983). *J. Chem. Soc. Dalton Trans.* pp. 657–664.

Warncke, G., Böhme, U., Günther, B. & Kronstein, M. (2012). *Polyhedron*, **47**, 46–52.

## Table 3
Experimental details.

| | |
|---|---|
| **Crystal data** | |
| Chemical formula | $C_{24}H_{36}N_4O_6Si_2$ |
| $M_r$ | 532.75 |
| Crystal system, space group | Monoclinic, $I2/c$ |
| Temperature (K) | 153 |
| $a$, $b$, $c$ (Å) | 12.9641 (8), 16.8966 (7), 13.1085 (8) |
| $\beta$ (°) | 101.198 (5) |
| $V$ (Å$^3$) | 2816.7 (3) |
| $Z$ | 4 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.17 |
| Crystal size (mm) | $0.40 \times 0.33 \times 0.15$ |
| | |
| **Data collection** | |
| Diffractometer | Stoe IPDS 2T |
| Absorption correction | Integration (*X-RED*; Stoe, 2009) |
| $T_{min}$, $T_{max}$ | 0.907, 0.993 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 19293, 3242, 2833 |
| $R_{int}$ | 0.039 |
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.650 |
| | |
| **Refinement** | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.032, 0.082, 1.08 |
| No. of reflections | 3242 |
| No. of parameters | 169 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.32, −0.23 |

Computer programs: *X-AREA* and *X-RED* (Stoe, 2009), *SHELXS* (Sheldrick, 2008), *SHELXL2017/1* (Sheldrick, 2015) and *ORTEP-3 for Windows* (Farrugia, 2012).

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**Computing details**

Data collection: *X-AREA* (Stoe, 2009); cell refinement: *X-AREA* (Stoe, 2009); data reduction: *X-RED* (Stoe, 2009); program(s) used to solve structure: *SHELXS* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2017/1* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *SHELXL2017/1* (Sheldrick, 2015).

**(8*E*,22*E*)-4,4,12,18,18,26-Hexamethyl-3,5,17,19-tetraoxa-8,13,22,27-tetraaza-4,18-disilatricyclo[22.4.0.0$^{10,15}$]octacosa-1(24),8,10,12,14,22,25,27-octaene-11,25-diol**

*Crystal data*

| | |
|---|---|
| $C_{24}H_{36}N_4O_6Si_2$ | $F(000) = 1136$ |
| $M_r = 532.75$ | $D_x = 1.256$ Mg m$^{-3}$ |
| Monoclinic, $I2/c$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $a = 12.9641$ (8) Å | Cell parameters from 19293 reflections |
| $b = 16.8966$ (7) Å | $\theta = 3.2$–28.8° |
| $c = 13.1085$ (8) Å | $\mu = 0.17$ mm$^{-1}$ |
| $\beta = 101.198$ (5)° | $T = 153$ K |
| $V = 2816.7$ (3) Å$^3$ | Prism, yellow |
| $Z = 4$ | $0.40 \times 0.33 \times 0.15$ mm |

*Data collection*

| | |
|---|---|
| Stoe IPDS 2T diffractometer | $T_{min} = 0.907$, $T_{max} = 0.993$ |
| Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus | 19293 measured reflections |
| | 3242 independent reflections |
| | 2833 reflections with $I > 2\sigma(I)$ |
| Plane graphite monochromator | $R_{int} = 0.039$ |
| Detector resolution: 6.67 pixels mm$^{-1}$ | $\theta_{max} = 27.5°$, $\theta_{min} = 2.0°$ |
| rotation method scans | $h = -16 \rightarrow 16$ |
| Absorption correction: integration (X-RED; Stoe, 2009) | $k = -21 \rightarrow 21$ |
| | $l = -16 \rightarrow 16$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Hydrogen site location: mixed |
| Least-squares matrix: full | H atoms treated by a mixture of independent and constrained refinement |
| $R[F^2 > 2\sigma(F^2)] = 0.032$ | |
| $wR(F^2) = 0.082$ | $w = 1/[\sigma^2(F_o^2) + (0.0343P)^2 + 2.1897P]$ |
| $S = 1.08$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 3242 reflections | $(\Delta/\sigma)_{max} = 0.001$ |
| 169 parameters | $\Delta\rho_{max} = 0.32$ e Å$^{-3}$ |
| 0 restraints | $\Delta\rho_{min} = -0.23$ e Å$^{-3}$ |

*Special details*

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

|  | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Si1 | 0.86455 (3) | 0.32645 (2) | −0.02263 (2) | 0.02075 (10) |
| O1 | 0.71097 (8) | 0.39251 (6) | 0.42399 (7) | 0.0296 (2) |
| H1 | 0.7514 (16) | 0.3499 (12) | 0.4190 (14) | 0.044* |
| O2 | 0.80401 (7) | 0.38781 (5) | 0.04330 (7) | 0.02281 (19) |
| O3 | 1.06149 (7) | 0.27321 (5) | 0.43122 (7) | 0.02520 (19) |
| N1 | 0.67254 (9) | 0.55915 (7) | 0.24920 (9) | 0.0294 (2) |
| N2 | 0.83696 (8) | 0.29351 (6) | 0.35941 (8) | 0.0230 (2) |
| C1 | 0.66458 (10) | 0.51009 (8) | 0.32707 (10) | 0.0259 (3) |
| C2 | 0.72289 (10) | 0.43890 (7) | 0.34287 (9) | 0.0233 (2) |
| C3 | 0.78833 (9) | 0.41735 (7) | 0.27376 (9) | 0.0209 (2) |
| C4 | 0.79399 (10) | 0.46943 (7) | 0.19053 (9) | 0.0229 (2) |
| C5 | 0.73609 (11) | 0.53867 (8) | 0.18313 (10) | 0.0282 (3) |
| H5 | 0.741329 | 0.574080 | 0.128082 | 0.034* |
| C6 | 0.58959 (11) | 0.53139 (9) | 0.39701 (11) | 0.0338 (3) |
| H6A | 0.629045 | 0.540267 | 0.467780 | 0.051* |
| H6B | 0.539444 | 0.488047 | 0.397491 | 0.051* |
| H6C | 0.551402 | 0.579715 | 0.371352 | 0.051* |
| C7 | 0.84345 (9) | 0.34072 (7) | 0.28447 (9) | 0.0206 (2) |
| H7 | 0.884566 | 0.326031 | 0.234897 | 0.025* |
| C8 | 0.85625 (10) | 0.45009 (7) | 0.10775 (10) | 0.0252 (3) |
| H8A | 0.861902 | 0.497621 | 0.065010 | 0.030* |
| H8B | 0.928130 | 0.433117 | 0.140566 | 0.030* |
| C9 | 0.89177 (10) | 0.21754 (7) | 0.36341 (10) | 0.0236 (2) |
| H9A | 0.914711 | 0.208345 | 0.296627 | 0.028* |
| H9B | 0.843029 | 0.174374 | 0.373348 | 0.028* |
| C10 | 0.98674 (10) | 0.21622 (7) | 0.45164 (10) | 0.0248 (3) |
| H10A | 0.964942 | 0.228849 | 0.518104 | 0.030* |
| H10B | 1.018780 | 0.162825 | 0.457622 | 0.030* |
| C11 | 0.94958 (13) | 0.38050 (10) | −0.09824 (13) | 0.0406 (4) |
| H11A | 0.907504 | 0.419996 | −0.142798 | 0.061* |
| H11B | 0.979557 | 0.342955 | −0.141483 | 0.061* |
| H11C | 1.006491 | 0.407029 | −0.050283 | 0.061* |
| C12 | 0.76208 (11) | 0.26635 (8) | −0.10486 (10) | 0.0284 (3) |
| H12A | 0.717809 | 0.241394 | −0.061306 | 0.043* |
| H12B | 0.795342 | 0.225328 | −0.140318 | 0.043* |
| H12C | 0.718640 | 0.300404 | −0.156636 | 0.043* |

*Atomic displacement parameters (Å²)*

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Si1 | 0.02231 (17) | 0.02191 (17) | 0.01900 (16) | 0.00084 (12) | 0.00636 (12) | 0.00114 (12) |
| O1 | 0.0360 (5) | 0.0297 (5) | 0.0259 (4) | 0.0028 (4) | 0.0128 (4) | 0.0013 (4) |
| O2 | 0.0232 (4) | 0.0221 (4) | 0.0228 (4) | −0.0002 (3) | 0.0034 (3) | −0.0036 (3) |
| O3 | 0.0241 (4) | 0.0287 (5) | 0.0230 (4) | −0.0076 (4) | 0.0054 (3) | −0.0008 (3) |
| N1 | 0.0338 (6) | 0.0237 (5) | 0.0288 (5) | 0.0025 (4) | 0.0011 (4) | −0.0044 (4) |
| N2 | 0.0219 (5) | 0.0229 (5) | 0.0237 (5) | −0.0010 (4) | 0.0029 (4) | 0.0000 (4) |
| C1 | 0.0251 (6) | 0.0259 (6) | 0.0254 (6) | −0.0010 (5) | 0.0012 (5) | −0.0074 (5) |
| C2 | 0.0240 (6) | 0.0240 (6) | 0.0209 (5) | −0.0033 (5) | 0.0020 (4) | −0.0039 (4) |
| C3 | 0.0214 (5) | 0.0206 (5) | 0.0195 (5) | −0.0040 (4) | 0.0011 (4) | −0.0031 (4) |
| C4 | 0.0264 (6) | 0.0203 (6) | 0.0211 (5) | −0.0049 (4) | 0.0026 (4) | −0.0033 (4) |
| C5 | 0.0374 (7) | 0.0213 (6) | 0.0246 (6) | −0.0017 (5) | 0.0026 (5) | −0.0019 (5) |
| C6 | 0.0283 (7) | 0.0370 (7) | 0.0363 (7) | 0.0046 (6) | 0.0072 (5) | −0.0080 (6) |
| C7 | 0.0200 (5) | 0.0218 (6) | 0.0196 (5) | −0.0030 (4) | 0.0024 (4) | −0.0033 (4) |
| C8 | 0.0306 (6) | 0.0210 (6) | 0.0246 (6) | −0.0058 (5) | 0.0071 (5) | −0.0014 (4) |
| C9 | 0.0237 (6) | 0.0203 (6) | 0.0263 (6) | −0.0027 (4) | 0.0034 (5) | −0.0003 (4) |
| C10 | 0.0229 (6) | 0.0231 (6) | 0.0280 (6) | −0.0032 (5) | 0.0040 (5) | 0.0049 (5) |
| C11 | 0.0394 (8) | 0.0453 (9) | 0.0415 (8) | −0.0018 (7) | 0.0192 (7) | 0.0115 (7) |
| C12 | 0.0370 (7) | 0.0264 (6) | 0.0204 (6) | −0.0002 (5) | 0.0024 (5) | −0.0014 (5) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Si1—O2 | 1.6435 (9) | C5—H5 | 0.9500 |
| Si1—O3ⁱ | 1.6487 (9) | C6—H6A | 0.9800 |
| Si1—C12 | 1.8443 (14) | C6—H6B | 0.9800 |
| Si1—C11 | 1.8589 (15) | C6—H6C | 0.9800 |
| O1—C2 | 1.3539 (15) | C7—H7 | 0.9500 |
| O1—H1 | 0.90 (2) | C8—H8A | 0.9900 |
| O2—C8 | 1.4345 (14) | C8—H8B | 0.9900 |
| O3—C10 | 1.4278 (14) | C9—C10 | 1.5168 (17) |
| N1—C1 | 1.3343 (18) | C9—H9A | 0.9900 |
| N1—C5 | 1.3512 (18) | C9—H9B | 0.9900 |
| N2—C7 | 1.2808 (16) | C10—H10A | 0.9900 |
| N2—C9 | 1.4631 (16) | C10—H10B | 0.9900 |
| C1—C2 | 1.4143 (18) | C11—H11A | 0.9800 |
| C1—C6 | 1.5039 (18) | C11—H11B | 0.9800 |
| C2—C3 | 1.4041 (17) | C11—H11C | 0.9800 |
| C3—C4 | 1.4147 (17) | C12—H12A | 0.9800 |
| C3—C7 | 1.4723 (17) | C12—H12B | 0.9800 |
| C4—C5 | 1.3832 (18) | C12—H12C | 0.9800 |
| C4—C8 | 1.5085 (17) | | |
| | | | |
| O2—Si1—O3ⁱ | 103.40 (5) | N2—C7—H7 | 119.4 |
| O2—Si1—C12 | 106.94 (6) | C3—C7—H7 | 119.4 |
| O3ⁱ—Si1—C12 | 112.06 (6) | O2—C8—C4 | 108.98 (10) |
| O2—Si1—C11 | 111.33 (7) | O2—C8—H8A | 109.9 |

| | | | |
|---|---|---|---|
| O3<sup>i</sup>—Si1—C11 | 109.52 (6) | C4—C8—H8A | 109.9 |
| C12—Si1—C11 | 113.16 (7) | O2—C8—H8B | 109.9 |
| C2—O1—H1 | 104.4 (12) | C4—C8—H8B | 109.9 |
| C8—O2—Si1 | 123.61 (8) | H8A—C8—H8B | 108.3 |
| C10—O3—Si1<sup>i</sup> | 123.50 (8) | N2—C9—C10 | 110.90 (10) |
| C1—N1—C5 | 118.59 (11) | N2—C9—H9A | 109.5 |
| C7—N2—C9 | 118.05 (11) | C10—C9—H9A | 109.5 |
| N1—C1—C2 | 121.46 (12) | N2—C9—H9B | 109.5 |
| N1—C1—C6 | 118.23 (12) | C10—C9—H9B | 109.5 |
| C2—C1—C6 | 120.30 (12) | H9A—C9—H9B | 108.0 |
| O1—C2—C3 | 122.14 (11) | O3—C10—C9 | 109.10 (10) |
| O1—C2—C1 | 117.91 (11) | O3—C10—H10A | 109.9 |
| C3—C2—C1 | 119.92 (11) | C9—C10—H10A | 109.9 |
| C2—C3—C4 | 117.69 (11) | O3—C10—H10B | 109.9 |
| C2—C3—C7 | 120.63 (11) | C9—C10—H10B | 109.9 |
| C4—C3—C7 | 121.57 (11) | H10A—C10—H10B | 108.3 |
| C5—C4—C3 | 118.12 (12) | Si1—C11—H11A | 109.5 |
| C5—C4—C8 | 119.45 (11) | Si1—C11—H11B | 109.5 |
| C3—C4—C8 | 122.36 (11) | H11A—C11—H11B | 109.5 |
| N1—C5—C4 | 124.19 (12) | Si1—C11—H11C | 109.5 |
| N1—C5—H5 | 117.9 | H11A—C11—H11C | 109.5 |
| C4—C5—H5 | 117.9 | H11B—C11—H11C | 109.5 |
| C1—C6—H6A | 109.5 | Si1—C12—H12A | 109.5 |
| C1—C6—H6B | 109.5 | Si1—C12—H12B | 109.5 |
| H6A—C6—H6B | 109.5 | H12A—C12—H12B | 109.5 |
| C1—C6—H6C | 109.5 | Si1—C12—H12C | 109.5 |
| H6A—C6—H6C | 109.5 | H12A—C12—H12C | 109.5 |
| H6B—C6—H6C | 109.5 | H12B—C12—H12C | 109.5 |
| N2—C7—C3 | 121.19 (11) | | |
| | | | |
| O3<sup>i</sup>—Si1—O2—C8 | 68.47 (10) | C2—C3—C4—C8 | −176.10 (11) |
| C12—Si1—O2—C8 | −173.10 (9) | C7—C3—C4—C8 | 0.08 (17) |
| C11—Si1—O2—C8 | −49.03 (11) | C1—N1—C5—C4 | 0.17 (19) |
| C5—N1—C1—C2 | 1.61 (18) | C3—C4—C5—N1 | −1.42 (19) |
| C5—N1—C1—C6 | −176.99 (12) | C8—C4—C5—N1 | 175.64 (12) |
| N1—C1—C2—O1 | 179.60 (11) | C9—N2—C7—C3 | 178.48 (10) |
| C6—C1—C2—O1 | −1.83 (17) | C2—C3—C7—N2 | −3.14 (17) |
| N1—C1—C2—C3 | −2.09 (18) | C4—C3—C7—N2 | −179.21 (11) |
| C6—C1—C2—C3 | 176.48 (11) | Si1—O2—C8—C4 | −154.64 (8) |
| O1—C2—C3—C4 | 179.01 (11) | C5—C4—C8—O2 | −106.34 (13) |
| C1—C2—C3—C4 | 0.78 (17) | C3—C4—C8—O2 | 70.59 (14) |
| O1—C2—C3—C7 | 2.80 (17) | C7—N2—C9—C10 | 108.51 (12) |
| C1—C2—C3—C7 | −175.43 (10) | Si1<sup>i</sup>—O3—C10—C9 | 143.92 (9) |
| C2—C3—C4—C5 | 0.87 (16) | N2—C9—C10—O3 | −65.04 (13) |
| C7—C3—C4—C5 | 177.05 (11) | | |

Symmetry code: (i) −*x*+2, *y*, −*z*+1/2.

*Hydrogen-bond geometry (Å, º)*

$Cg1$ is the centroid of the N1/C1–C5 ring.

| $D$—H⋯$A$ | $D$—H | H⋯$A$ | $D$⋯$A$ | $D$—H⋯$A$ |
|---|---|---|---|---|
| O1—H1⋯N2 | 0.90 (2) | 1.76 (2) | 2.5923 (15) | 153.2 (18) |
| C5—H5⋯O1[ii] | 0.95 | 2.69 | 3.5451 (16) | 151 |
| C6—H6$A$⋯O2[iii] | 0.98 | 2.59 | 3.3464 (17) | 134 |
| C7—H7⋯O3[i] | 0.95 | 2.57 | 3.4882 (15) | 162 |
| C9—H9$B$⋯O2[iv] | 0.99 | 2.60 | 3.5087 (16) | 153 |
| C9—H9$B$⋯$Cg1$[iv] | 0.99 | 3.31 | 4.039 (2) | 131 |
| C11—H11$A$⋯$Cg1$[ii] | 0.98 | 2.85 | 3.7880 (2) | 160 |

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