Zeitschrift für Kristallographie 166, 11–22 (1984)
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Studies on clathrasils. IV*

Crystal structure of dodecasil 1H, a synthetic clathrate compound of silica**

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Received: March 2, 1983

Crystal structure / Silica clathrate

Abstract. Synthetic dodecasil 1 H, $34\,SiO_2 \cdot 3\,M^{12} \cdot 2\,M^{12'} \cdot 1\,M^{20}$, with M^{12} and $M^{12'} = N_2$ and M^{20} = piperidine, is hexagonal with space group $P6/mmm$ and $a = 13.783(4)$ and $c = 11.190(3)$ Å. Structure refinement with 658 independent reflexions led to a weighted $R_w = 0.056$. The clathrate compound has a silica host framework and organic guest molecules M within three different types of cages. It is the simplest member (1-layer polytype) of the polytypic series of dodecasils. Corner sharing [SiO_4] tetrahedra form a 3-dimensional 4-connected net which is built up from hexagonal layers of face sharing pentagondodecahedra ([5^{12}] cages), the fundamental cage of the dodecasil series. Connecting such layers in sequence $\bar{A}A$ two new types of cagelike voids arise, the [$4^3 5^6 6^3$] cage and the [$5^{12} 6^8$] cage. The guest molecules M^{12}, $M^{12'}$ and M^{20}, which must be present during synthesis, show up in difference Fourier syntheses. The entrapped molecules are oriented within the cages such that van der Waals contacts between guest molecules and host framework are optimized. The mean value of the Si – O – Si angles (170.6°) is considerably higher and the mean value of Si – O distances (1.565 Å) is considerably lower than corresponding angles and distances of silica polymorphs.

Introduction

The wide range of structural analogy between polymorphs of ice and silica has recently been extended to clathrate compounds (Kamb, 1965; Schlenker et al., 1981). Syntheses and structure refinements of melanophlogite and

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* Part III of this series: Gies (1983)

** Parts of these studies have been presented at the 22. Diskussionstagung der AGKr, Kiel, 1982 (Gerke et al., 1982) dodecasil 3C, which are isostructural with the cubic gas hydrates of type I and type II respectively (Gies et al., 1982a; Gies, 1983; Gies et al., 1982b) have been reported in parts I to III of this series. We report here on dodecasil 1H, the first synthetic clathrasil with an SiO_2 framework unknown in clathrate hydrate chemistry.

Experimental

Crystals were synthesized under hydrothermal conditions from aqueous solutions of silicic acid in presence of N_2 and piperidine as guest molecules at 250 °C. A hexagonal prismatic crystal (edge: 0.17 mm, thickness: 0.15 mm) was selected for X-ray data collection on a Philips PW 1100 automatic four circle diffractometer using graphite monochromatized Mo$K\alpha$ radiation ($\lambda = 0.7107$ Å) and $\omega - 2\theta$ scan ($\theta_{max} = 30°$). The intensities of 5811 reflexions were recorded; by averaging symmetry equivalent intensities 1102 unique reflexions were obtained $\left(R = \sqrt{\frac{\Sigma N(\Sigma \bar{F} - F)^2 \cdot w}{\Sigma (N - I) \Sigma w \cdot F^2}} = 0.0323\right)$; 658 of them had $|F_o| \geq 6\sigma(|F_o|)$. The standard deviations $\sigma(F_o)$ were estimated using the formula cited by Stout and Jensen (1968). No corrections for absorption seemed to be necessary ($\mu = 6.18\,\mathrm{cm}^{-1}$). The calculations for structure refinement were performed with the SHELX-76 system (Sheldrick, 1976). Refined cell parameters were determined with the program LAT (Hornstra and Vossers, 1973/74). The scattering factors were taken from International Tables for X-ray Crystallography, Vol. IV, 1974, for neutral atoms.

Results of structure refinement

The proposal for the crystal structure of dodecasil 1H was derived by comparing the cell parameters of dodecasil 3C (Gies et al., 1982b) and the title compound [$a(3C) = 19.4$ Å, $a(1H) = \frac{1}{2}\sqrt{2} \cdot a(3C)$; $c(1H) = \frac{1}{3} \cdot \sqrt{3a^2(3C)}$. The structure refinement was performed in space group $P6/mmm$ with refined cell parameters $a = 13.783(4)$ Å and $c = 11.190(3)$ Å, using a set of fractional coordinates obtained from a tetrapod model. Anisotropic refinement of the host SiO_2 framework converged at $R = 0.175$, $R_w = 0.106$ $\left(R_w = \frac{\Sigma(|F_o| - |F_c|) \cdot \sqrt{w}}{\Sigma |F_o| \cdot \sqrt{w}}\right)$ using all 1102 reflexions whereas the smaller data set with $|F_o| \geqq 6\sigma$ ($|F_o|$) led to $R' = 0.098$, $R'_w = 0.086$. By considering guest molecules located within the host framework cages as described later residuals improved to $R = 0.162$, $R_w = 0.077$ and $R' = 0.079$, $R'_w = 0.056$, respectively. Final results, atomic parameters, angles and distances are listed in Tables 1 and 2. A list of observed and calculated structure factors can be obtained from the authors.

Table 1. Atomic parameters and thermal parameters U_{ij} [Å^2] with standard deviation $\left(\text{temperature factors of the form } \exp[-2\pi^2(U_{11} \cdot h_2 \cdot a^{*2} + \ldots 2\,U_{12}hka^*b^*)],\ B = 8\pi^2\left(\frac{U_{11}+U_{22}+U_{33}}{3}\right)\right)$

Atom	No. of positions	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	B_{eq}
Si(1)	12	0.4186(2)	0.2093(1)	0.2252(2)	0.0228(11)	0.0218(18)	0.0238(10)	−0.0090(19)	−0.0045(10)	0.0109(9)	1.784
Si(2)	12	0.3868(1)	0.0000(0)	0.3627(2)	0.0323(9)	0.0319(12)	0.0256(11)	0.0000(0)	−0.0076(9)	0.0159(6)	2.363
Si(3)	6	0.2628(2)	0.1314(1)	0.0000(0)	0.0160(15)	0.0220(11)	0.0238(15)	0.0000(0)	0.0000(0)	0.0080(7)	1.627
Si(4)	4	0.3333(0)	0.6667(0)	0.1384(3)	0.0289(13)	0.0289(13)	0.0164(19)	0.0000(0)	0.0000(0)	0.0144(6)	1.953
O(1)	24	0.1052(3)	0.3933(4)	0.3031(4)	0.0619(29)	0.1152(39)	0.7570(30)	0.0047(33)	0.0350(27)	0.0585(29)	6.672
O(2)	12	0.5429(4)	0.2715(2)	0.8164(7)	0.0229(31)	0.0805(37)	0.1012(56)	−0.0049(17)	−0.0097(35)	0.0114(15)	5.393
O(3)	12	0.3405(5)	0.1702(2)	0.1139(5)	0.0536(37)	0.0761(32)	0.0367(33)	0.0000(0)	0.0000(0)	0.0268(19)	4.358
O(4)	6	0.3601(5)	0.0000(0)	0.5000(0)	0.0627(39)	0.0959(71)	0.0121(34)	0.0000(0)	0.0000(0)	0.0479(36)	4.553
O(5)	6	0.1865(6)	0.0000(0)	0.0000(0)	0.0418(38)	0.0132(38)	0.0970(68)	0.0000(0)	0.0000(0)	0.0066(19)	4.006
O(6)	6	0.5000(0)	0.0000(0)	0.3451(8)	0.0610(37)	0.1523(96)	0.0621(62)	0.0000(0)	0.0000(0)	0.0762(48)	7.240
O(7)	2	0.3333(0)	0.6667(0)	0.0000(0)	0.1735(145)	0.1735(145)	0.0382(115)	0.0000(0)	0.0000(0)	0.0868(73)	10.064

Table 2. Interatomic distances in Å and angles in degrees with standard deviations in the SiO_2 host framework of dodecasil 1H

Si(1)–O(1)	1.562(6)	2×	O(1)–Si(1)–O(1)	107.6(5)		O(1)–O(1)	2.521(13)	
–O(2)	1.556(7)		O(1)– –O(2)	110.5(3)	2×	O(1)–O(2)	2.562(8)	2×
–O(3)	1.556(7)		O(1)– –O(3)	109.4(2)	2×	O(1)–O(3)	2.545(8)	2×
average	1.559		O(2)– –O(3)	109.5(4)		O(2)–O(3)	2.541(9)	
			average	109.5		average	2.546	
Si(2)–O(1)	1.558(6)	2×	O(1)–Si(2)–O(1)	107.5(4)		O(1)–O(1)	2.513(10)	
–O(4)	1.580(3)		O(1)– –O(4)	108.7(3)	2×	O(1)–O(4)	2.550(5)	2×
–O(6)	1.572(3)		O(1)– –O(6)	110.5(3)	2×	O(1)–O(6)	2.572(8)	2×
average	1.567		O(4)– –O(6)	110.6(5)		O(4)–O(6)	2.592(10)	
			average	109.4		average	2.558	
Si(3)–O(3)	1.575(7)	2×	O(3)–Si(3)–O(3)	107.9(5)	2×	O(3)–O(3)	2.547(13)	2×
–O(5)	1.575(2)	2×	O(3)– –O(5)	109.9(2)	2×	O(3)–O(5)	2.579(7)	2×
average	1.575		O(5)– –O(5)	109.3(7)	2×	O(5)–O(5)	2.570(9)	2×
			average	109.0		average	2.565	
Si(4)–O(2)	1.561(6)	3×	O(2)–Si(4)–O(2)	110.0(3)	3×	O(2)–O(2)	2.558(10)	3×
–O(7)	1.549(4)		O(2)– –O(7)	108.9(3)	3×	O(2)–O(7)	2.531(8)	3×
average	1.558		average	109.5		average	2.545	
mean value	1.565		mean value	109.38		mean value	2.554	

Si(2)–O(1)–Si(1)	167.7(5)	24×	Si(3)–O(5)–Si(3)	169.3(7)	6×
Si(1)–O(2)–Si(4)	178.4(7)	12×	Si(2)–O(6)–Si(2)	165.7(8)	6×
Si(1)–O(3)–Si(3)	179.2(5)	12×	Si(4)–O(7)–Si(4)	180.0(0)	2×
Si(2)–O(4)–Si(2)	153.0(7)	6×	mean value	170.6	

Description of the structure

[SiO_4] tetrahedra are corner-linked to build a 3-dimensional 4-connected silica network in the sense of Wells (1975). The host lattice can completely be set up by pentagondodecahedra ([5^{12}]-cages), the fundamental cage of the dodecasil polytype series. Each [5^{12}] cage shares faces with 4 other [5^{12}] cages to form layers of hexagonal symmetry (Fig. 1). The layers are connected by common oxygen atoms and stacked with layer sequence $\bar{A}A$. Such sequence, which is unknown in hard sphere packing models, results in a single-layer polytype as simplest member of a polytype series. In addition to the [5^{12}] cages within the layers, two other types of cages, two [$4^3 5^6 6^3$] cages and one [$5^{12}6^8$] cage per unit cell, are formed when stacking the layer as described (Fig. 2).

The mean values of 170.6° for the Si–O–Si angles and 1.565 Å for the Si–O distances of the SiO_2 host framework of dodecasil 1H (Table 2) differ considerably from those of the known silica polymorphs but are comparable with the corresponding mean values found in melanophlogite. The grand

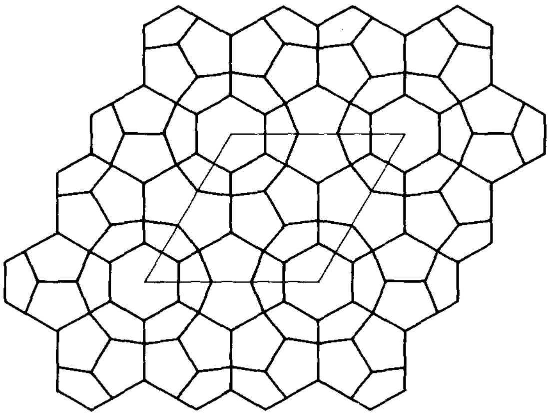


Fig. 1. Projection of the hexagonal layer shown as net of the silicon atoms. The oxygen atoms are located near to the middle of each Si–Si bond

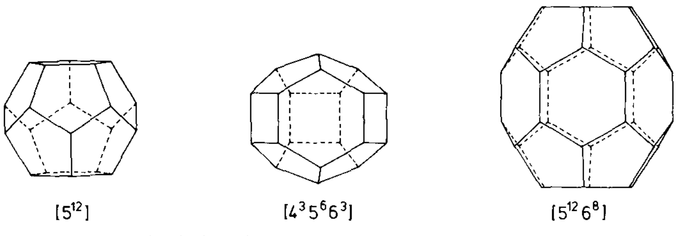


Fig. 2. Cage types present in dodecasil 1H

mean value of 144° for Si – O – Si angles reported by Tossel and Gibbs (1978) is considerably lower than the mean values 168.8° of melanophlogite (Gies, 1983) and 170.6° of dodecasil 1 H. The grand mean value 1.608 Å reported by Brown and Gibbs (1969) for Si – O distances in silica frameworks is considerably higher than the mean values 1.576 Å for melanophlogite (Gies, 1983) and 1.565 Å for dodecasil 1H. In agreement with the correlation reported by Hill and Gibbs (1979) between Si – O distances and Si – O – Si angles in silica polymorphs the very high mean value $\langle \sphericalangle(\mathrm{Si-O-Si}) \rangle$ in dodecasil 1H involves a very low mean value $\langle d(\mathrm{Si-O}) \rangle$, as already confirmed for melanophlogite.

The unusually short Si – O distances and high Si – O – Si angles obtained for melanophlogite and dodecasil 1H are associated with unusually large temperature factors of the oxygen atoms and can therefore partly be interpreted as due to static or dynamic disorder (Liebau, 1983).

Guest molecules

Heights and positions of maxima in difference Fourier syntheses $\varrho_{\mathrm{obs}} - \varrho_{\mathrm{calc(Si,O)}}$ within the cages strongly support the suggestion that the guest molecules are enclathrated. With regard to size and shape, the guest molecules $M^{12'}$, M^{12} and M^{20} of dodecasil 1H, which are entrapped within the three types of cages $[4^3 5^6 6^3]$, $[5^{12}]$ and $[5^{12} 6^8]$ respectively can be subdivided into two groups. The small dodecahedra house guest molecules with van der Waals diameter up to about 5.7 Å; the void of the icosahedron $[5^{12} 6^8]$ can be described by an ellipsoid with $d_1 \simeq 11$ Å, $d_2 \simeq 7.7$ Å and $d_3 \simeq 7.7$ Å, large enough to house guest molecules with up to 28 atoms (1-adamantylamine $C_{10}H_{15} \cdot NH_2$). Based on the specific conditions during the synthesis of the crystal and on mass spectroscopic analyses for the crystal investigated only molecular nitrogen N_2 and piperidine $C_5H_{10}NH$ as guest molecules have been taken into consideration.

The difference Fourier map shows 17 distinct residual electron density maxima within the void of the $[4^3 5^6 6^3]$ cage (site symmetry of cage centre: $\bar{6}m2$) (Table 3), which belong to four crystallographically different sites S1 to

Table 3. Positions and heights of the residual electron density maxima found in the $[4^3 5^6 6^3]$ cage

Maximum	x	y	z	Maxima per cage	Maximum height e/Å^3
S1	0.333	0.667	0.356	2	2.2
S2	0.381	0.762	0.402	6	1.5
S3	0.309	0.618	0.436	6	2.1
S4	0.230	0.760	0.500	3	1.4

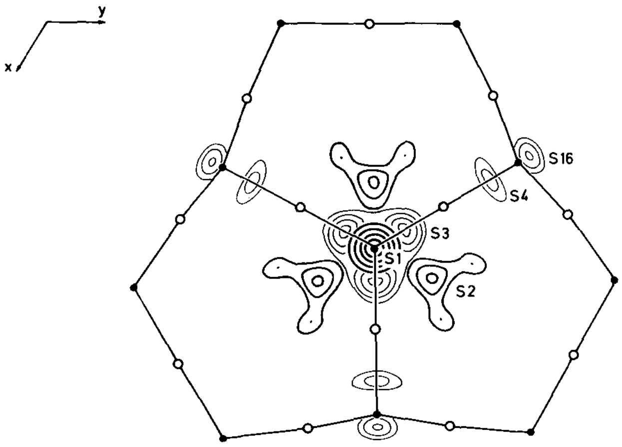


Fig. 3. Composite map of the residual electron density maxima in the $[4^35^66^3]$ cage of dodecasil 1H. Isolines show in steps of 0.5 electrons/Å^3 clouds of the residual electron densities (first line =0.5 e/Å^3)

S4. No maximum in the centre of the cage has been found. In Figure 3 a projection parallel [001] of the residual electron density maxima in one half of the $[4^35^66^3]$ cage is shown. The positions of the maxima reveal that the guest molecules incorporated are not fully disordered but occupy preferred orientations to optimize van der Waals contacts with the host framework (Table 6). The distances between the different maxima identify the guest molecule as N_2. Of all distances between the maxima S1 to S4 only the distances $d_{2,3} = 1.13$ Å between S2 to S3 and $d_{1,3} = 1.26$ Å between S1 to S3 are in good agreement with the distance $d_{N-N} = 1.098$ Å reported by Ondike and Smith (1968) for solid nitrogen. That means that one atom (S3) of each N_2 molecule in the $[4^35^66^3]$ cage is in contact with six oxygen atoms of a hexagon of the cage while the other N atom either has contact with five oxygen atoms of one five-membered ring (S2) or lies on the $\bar{6}$ axis through the cage centre to have contact with the three oxygen atoms bonded to the silicon atom at the top of the cage (S1). The maxima S4 which were found near the midpoint of the six-membered rings of the $[4^35^66^3]$ cage will be discussed later together with the guest molecules of the icosahedron.

The residual electron density within the slightly larger pentagondodecahedron $[5^{12}]$ (site symmetry of the cage centre: *mmm*) cannot clearly be subdivided into distinct maxima but only into three regions with different maxima. These may indicate that a greater proportion of the N_2 molecules incorporated is disordered than in the $[4^35^66^3]$ cage. The section $(x,y,0)$ through the cage centre in $0\frac{1}{2}0$ can be described as a discus with ten maxima (S6 – S8) in the plane *xy*0 and two maxima out of the plane (S5). There is no maximum in the cage centre (Table 4). In Figure 4 these twelve maxima are

Table 4. Positions heights of the residual electron density maxima in the $[5^{12}]$ cage

Maximum	x	y	z	Maxima per cage	Maxima height e/Å^3
S5	0	0.5	0.036	2	2.4
S6	0.092	0.636	0	4	1.6
S7	0.122	0.531	0	4	1.4
S8	0	0.431	0	2	1.3
S9	0.140	0.570	0.122	4	1.4

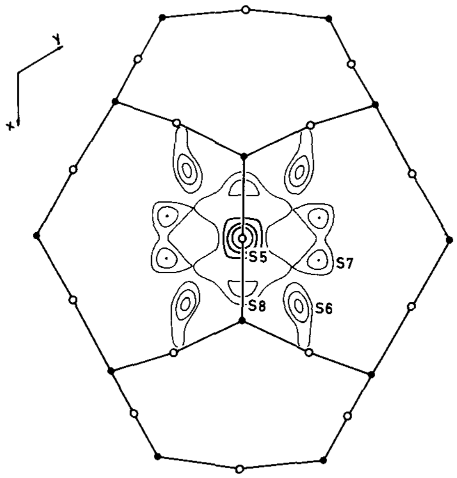


Fig. 4. Composite map of the residual electron density maxima in the $[5^{12}]$ cage. Isolines show in steps of 0.5 electrons/Å^3 the clouds of the residual electron densities (first line = 0.5 e/Å^3)

shown in projection parallel [001]. Above and below the discus two smaller clouds can be found with two distinct maxima each (S9). Their residual electron density maxima are located close to the five-membered ring shared with other $[5^{12}]$ cages of the same layer, while near the five-membered rings shared with the $[5^{12}6^8]$ cage between the layers no maximum could be registered. Distances between the centres of these maxima, which can be interpreted as positions of nitrogen atoms of the N_2 guest molecules, vary between 0.92 and 1.43 Å. The large deviations of the observed distances from the N – N distance reported by Ondik and Smith (1968) indicate that at least some of these maxima are superpositions of several split-atom positions due to higher degree of disorder of the guest molecules.

Within the large $[5^{12}6^8]$ cage (site symmetry of the cage centre: $6/mmm$) a large and structured residual electron density is to be seen. One can distinguish between three different regions of residual electron density, one

Table 5. Positions and heights of the residual electron density maxima in the $[5^{12}6^8]$ cage

Maximum	*x*	*y*	*z*	Maxima per cage	Maximum height e/Å^3
S10	0	0	0.296	2	2.5
S11	0.038	0.010	0.380	24	2.2
S12	0.040	0.080	0.458	12	2.1
S13	0.041	0.082	0.316	12	2.0
S14	0.085	0	0.398	12	1.9
S15	0	0	0.049	2	1.6
S16	0.199	0.398	0.462	12	1.6

Table 6. Distances between residual electron density maxima within the cages and the host framework interpreted as van der Waals contacts between host and guest

$[4^35^66^3]$ cage

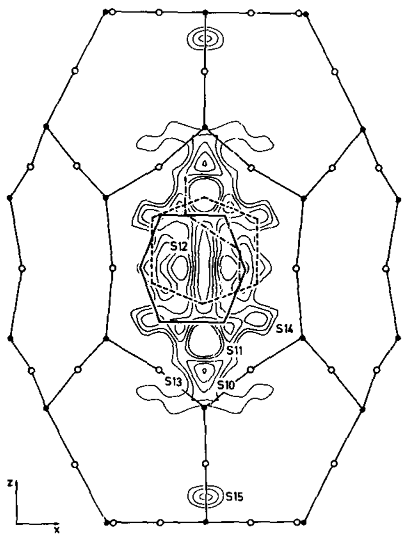
distance from			to	
S1			Si(4)	2.44
S2	O(1)	2.93	Si(1)	3.26
	O(2)	2.79	Si(2)	3.27
	O(6)	2.91	Si(4)	3.16
S3	O(1)	3.32	Si(1)	3.35
	O(2)	2.97	Si(4)	3.38
S4	O(1)	2.73	Si(1)	3.14
	O(4)	2.87	Si(2)	3.29
	O(4)	2.75	Si(2)	3.18

$[5^{12}]$ cage

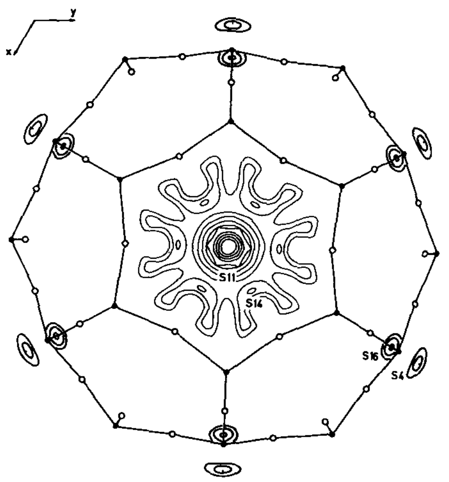
distance from			to	
S9	O(2)	2.14	Si(1)	2.93
	O(6)	3.01	Si(4)	2.32
	O(7)	2.68		

$[5^{12}6^8]$ cage

distance from			to	
S15	O(5)	2.63	Si(3)	3.19
S16	O(1)	2.18	Si(1)	2.66
	O(4)	2.56	Si(1)	3.51
			Si(2)	2.89
			Si(2)	3.32



a



b

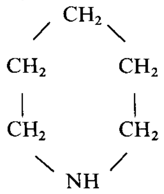
Fig. 5a. Section through the residual electron density of the $[5^{12}6^8]$ cage in the plane $(0,y,z)$. Three possible orientations of the guest molecule  are indicated. ($\Delta_{\text{isolines}} = 0.5$ electrons/Å^3, first line = 0.5 electrons/Å^3)

Fig. 5b. Section through the residual electron density of the $[5^{12}6^8]$ cage in the plane $(x,y,0.38)$. ($\Delta_{\text{isolines}} = 0.5$ electrons/Å^3, first line = 0.5 electrons/Å^3)

region around the centre of the cage with five non-equivalent maxima S10 – S14, a second region near the hexagon in $(xy0)$ S15 (Fig. 5a), and a third one near the hexagons parallel [001] shared with the $[4^35^66^3]$ cages, S16 (Table 5, Fig. 3 and 5b). The central part of the residual electron density within the cage represents piperidine as guest molecule. Analysing angles and distances between the different maxima it is possible to adapt three crystallographically different 6-fold disordered orientations of the guest molecule. In Figure 5a one example for each of the three different orientations of the guest molecule is indicated. The high degree of disorder implies that the electron densities of $3 \times 6 \times 6 = 108$ carbon and nitrogen atoms superimpose within a relatively small volume near the centre of the cage, i.e. the centre of each of the maxima shown in Figures 5a and b is not the true position of one guest molecule atom but a superposition of the electron densities of

Table 7. Distances of residual electron density maxima which are adapted for 3 orientations of the pyridine guest molecule within the $[5^{12}6^8]$ cage

Guest molecule	Distances of residual electron density maxima	
		Å
——	d(S14 – S11)	1.40
	d(S14 – S14)	2.34
	d(S14 – S12)	1.64
– – –	d(S14 – S14)	1.56
	d(S14 – S14)	2.34
·–·–·	d(S13 – S13)	1.78
	d(S14 – S12)	1.64
	d(S12 – S12)	1.65

several atoms. Consequently, some of the distances and angles between these maxima (Table 7) deviate considerably from bond lengths ($d_{C-C} = 1.54$ Å, $d_{C-N} = 1.47$ Å), and bond angles (109.4°) observed in typical aliphatic compounds (Kennard, 1968). In Table 7 the calculated distances for the three possible orientations are listed. The maxima within the cage are located near the six-membered rings as shown in Figure 5.

If one considers that the maximum free diameter of 2.8 Å (Barrer, 1968) of a six-membered ring formed by $[SiO_4]$ tetrahedra is large enough to let pass gases like helium, neon, hydrogen, nitrogen and oxygen and that the distances between S15 – S15 = 1.1 Å and S16 – S4 = 1.1 Å fit very well the theoretical $d_{N-N} = 1.098$ Å in nitrogen reported by Ondik and Smith (1968), then these maxima can be interpreted as N_2 molecules each lying in the centre of a six-membered ring and with their long molecular axes perpendicular to the plane of the ring. In this way the weak Lewis base N_2 is in close contact with six weak Lewis acid centres $[SiO_4]$ to form weak bonds in addition to van der Waals interactions. While the N_2 molecules are located in the centre of the six-membered rings common to the $[5^{12}6^8]$ cage and the $[4^35^66^3]$ cage, the orientation of the piperidine guest molecule within the large cage requires that the C – C bond parallel [001] of the guest molecule is in contact with the oxygen atoms of the Si – O – Si bonds parallel [001] in the equator of the $[5^{12}6^8]$ cage (Fig. 5).

For the structure refinement spherical scatterers (carbon atom) were used on the positions of the residual electron maxima S1 – S17 as listed in Tables 3 – 5. Only the central region of the $[5^{12}]$ cage was refined with one single scatterer instead of S5 to S8. Refinement of site occupation factors and isotropic temperature factors improved the residual as described above.

Structure refinement of other crystals of dodecasil 1H with other guest molecules are in general agreement with these results. A more elaborate analysis of the cage contents, however, shows characteristic variations. A more detailed study of cage contents of dodecasil 1 H with different guest molecules is in progress.

We thank Prof. F. Liebau for many helpful comments and fruitful discussions. We thank Prof. H. Küppers for critically reading the manuscript and U. Bennewitz for technical assistance.

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