# Solid-state N.M.R. Characterization of Clathrasils

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For two clathrasils both the crystallographically distinct silicon sites and the occluded organic species have been identified by cross-polarization magic-angle-spinning $^{29}Si$ and $^{13}C$ n.m.r. spectroscopy.

The well-known structural analogy between forms of $SiO_2$ and $H_2O$ has recently been shown to cover clathrate compounds as well. The mineral melanophlogite was found to be isostructural with the cubic gas hydrate I,[1] in accordance with an earlier

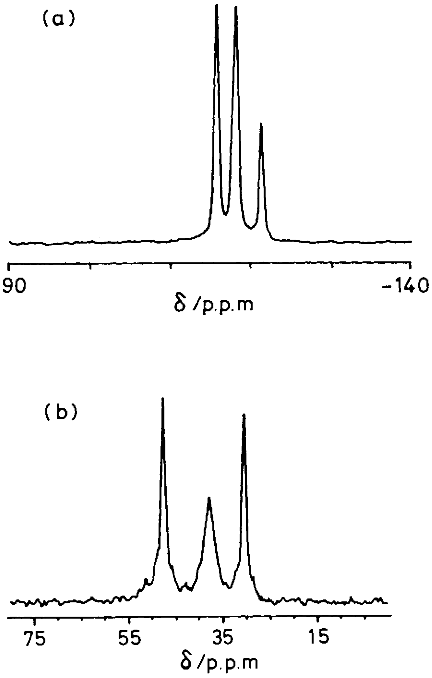

**Figure 1.** (a) C.p.m.a.s. $^{29}$Si n.m.r. spectrum of dodecasil-1H crystallized in the presence of 1-aminoadamantane; line widths of the δ −115.8, −118.1, and −121.3 p.p.m. lines are 37, 47, and 35 Hz, respectively. The spectrum was acquired using a Bruker CXP-300 n.m.r. spectrometer (7.05 T, 59.6 MHz). C.p. time 10 ms; recycle time 2 s; number of acquisitions 5000. M.a.s. was carried out in Beams–Andrew rotors fashioned from Delrin at 3.2 kHz. Chemical shifts are given with respect to liquid $Me_4Si$ (δ 0 p.p.m.) using $Q_8M_8$ as secondary external standard ($Me_3SiO$ peak δ 11.6 p.p.m.). (b) C.p.m.a.s. $^{13}$C n.m.r. spectrum of the same sample; resonances at δ 30.3, 37.9, and 47.5 p.p.m. The spectrum was acquired using a Bruker CXP-200 n.m.r. spectrometer (4.7 T, 50.3 MHz). Single c.p. contacts were employed using the flip-back and spin-temperature inversion sequences. C.p. time 2 ms; recycle time 2 s; number of acquisitions 37000. R.f. fields were 1.1 and 4.4 mT for the $^1$H and $^{13}$C channels, respectively. M.a.s. was carried out in Beams–Andrew rotors fashioned from coated boron nitride at 3.2 kHz. Chemical shifts are given with respect to liquid $Me_4Si$ (δ 0 p.p.m.).

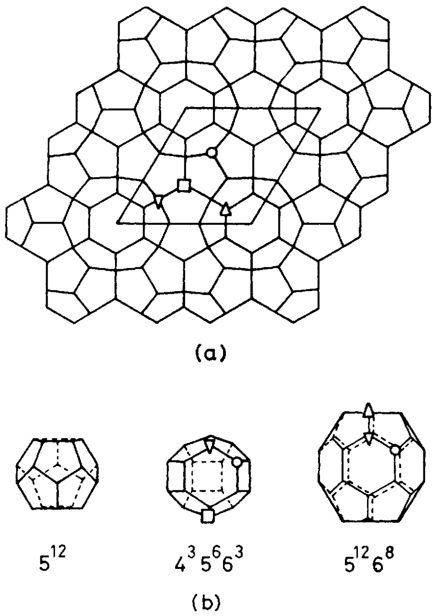

**Figure 2.** (a) The layer of face-sharing pentagonal dodecahedra. The dodecasil-1H structure corresponds to an AA.... stacking of such layers; unit cell as well as crystallographically distinguishable sites have been indicated: $T_1$ (○), $T_2$ (▽), $T_3$ (□), and $T_4$ (△). (b) Schematic representation of the three types of voids occurring in the dodecasil-1H structure.

proposal.[2] Gies *et al.* reported the first crystallization of silicates structurally related to clathrate hydrates, thereby disclosing a new class of synthetic silicates called clathrasils.[3] For dodecasil-1H and dodecasil-3C, two members of this family, the overall framework structure has been determined from *X*-ray diffraction.[3,4] Dodecasil-3C was found to be isostructural with the cubic gas hydrate II.

As these silicates are indeed clathrates, they possess characteristic cages: pentagonal dodecahedra, which are common to this type of clathrates, and larger cages that are specific for a particular structure. They crystallize in the presence of molecules that seem to play a structure-directing role and may become occluded in the cages.

The present preliminary communication deals with the structure of these silicates on the molecular level. We report the first solid-state $^{29}$Si and $^{13}$C n.m.r. spectroscopic investigation of two clathrasils, characterizing both their silicate network and the entrapped organic guest species.

Dodecasil-1H was synthesized from an aqueous solution of tetramethoxysilane hydrolysed with tetramethylammonium hydroxide.[3] After addition of 1-aminoadamantane the solution was hydrothermally treated under nitrogen for four days at 200 °C. The powder *X*-ray diffraction pattern was consistent with the published unit cell.[4] Elemental analysis yielded a Si content of 43.6 weight% and a low Al contamination of 350 p.p.m.

The cross-polarization magic-angle-spinning (c.p.m.a.s.) $^{29}$Si n.m.r. spectrum of this material is given in Figure 1(a). The spectrum consists of three narrow resonance lines. As compared to silicalite—a pentasil zeolite somewhat related to these clathrasils as regards its large number of five-rings—the resonances occur at rather low frequency.[5] The three lines point to crystallographically distinct tetrahedral silicon sites T in the dodecasil-1H structure. The intensity of the lines is strongly enhanced by c.p., but the intensity distribution between the lines is the same as without c.p. and is independent of the duration of c.p. (0.5—10 ms). Therefore we may regard the intensity ratio of 1.9:2.5:1 (for the δ −115.8, −118.1, and −121.3 p.p.m. resonances) as corresponding to the relative number of different silicon sites in the dodecasil-1H framework.

The structure of dodecasil-1H may be looked upon as composed of layers of face-sharing pentagonal dodecahedra ($5^{12}$) built from twenty corner-sharing [$SiO_4$] tetrahedra (Figure 2). These layers have six-fold symmetry. They are stacked right on top of each other (AA . . . sequence), which leads to hexagonal symmetry and two characteristic cages, *viz.* $4^3 5^6 6^3$ and $5^{12} 6^8$ polyhedra [Figure 2(b)]. In this structure four crystallographically different T sites exist, as indicated in Figure 2(a), in a ratio of 12($T_1$) : 12($T_2$) : 4($T_3$) : 6($T_4$) per unit cell. The intensity ratio of the three resonances in the $^{29}$Si n.m.r. spectrum being close to 12 : 16 : 6, we interpret these resonances as corresponding to the different T sites. The resonance at δ −121.3 p.p.m. can be unambiguously assigned to silicon in $T_4$ sites; the silicon in $T_3$ sites is responsible for part of the signal at δ −118.1 p.p.m. Unequivocal assignment of the resonances at δ −115.8 and −118.1 p.p.m. to sites $T_1$ and $T_2$ on the basis of spectral intensities and relative numbers of tetrahedral sites is impossible, however. We note that a silicon in a $T_1$ position is part of a four-ring whereas silicon in sites $T_2$ and $T_3$ is a member of five-rings (and a six-ring for $T_2$) but not of four-rings. This similarity of $T_2$ and $T_3$ leads us to suggest that the $\delta$ −115.8 p.p.m. resonance can be assigned to silicon in site $T_1$. Single crystal data for the atomic positions in dodecasil-1H would be of help to settle this ambiguity because of the observed correlation between mean Si–O–Si angle and $^{29}$Si n.m.r. chemical shifts for silica polymorphs.[6]

The c.p.m.a.s. $^{13}$C n.m.r. spectrum of this dodecasil-1H sample, given in Figure 1(b), reveals that intact 1-aminoadamantane is occluded in the silicate framework. The chemical shifts closely correspond to those observed in solution, which demonstrates that 1-aminoadamantane becomes accommodated in the cages without significant deformation or interaction with the framework. No more resonances are observed, indicating that no other organic species have been entrapped. The 1-aminoadamantane is almost certainly present in the $5^{12}6^8$ cages. These nearly spherical voids (*ca.* 0.83 × 0.95 nm) are the only ones large enough to accommodate 1-aminoadamantane (largest diameter *ca.* 0.8 nm).

Starting from the same synthesis mixture as for dodecasil-1H but adding trimethylamine instead of 1-aminoadamantane we obtained dodecasil-3C, as concluded from the powder *X*-ray diffraction pattern.[3,7] The cubic structure of dodecasil-3C corresponds to the ABC . . . stacking sequence of the same layers of pentagonal dodecahedra.

The c.p.m.a.s. $^{29}$Si n.m.r. spectrum of such a sample, although less well-resolved than the spectrum of dodecasil-1H, clearly shows three resonances at $\delta$ −112.6, −116.8, and −120.0 p.p.m. We attribute these lines to the three crystallographically distinct sites $T_1'$, $T_2'$ and $T_3'$ that are present in the dodecasil-3C structure.[7,8] The strongest resonance at $\delta$ −120.0 p.p.m. then corresponds to the most abundant silicon site $T_3'$, which closely resembles the $T_4$ site in the dodecasil-1H structure, while the resonance at $\delta$ −116.8 p.p.m. corresponds to site $T_2'$, which is similar to the $T_3$ site in dodecasil-1H. The occurrence of these resonances for dodecasil-3C at nearly the same frequencies as the corresponding ones for dodecasil-1H supports our interpretation of the $^{29}$Si n.m.r. spectra of these clathrasils.

In passing we note that the recently published $^{29}$Si n.m.r. spectrum of ZSM-39 (Si/Al = 54.3), an aluminosilicate structurally similar to dodecasil-3C,[7] shows three resonances as well, but at $\delta$ −109, −115, and −120 p.p.m.[9] These frequencies differ significantly from those found here for dodecasil-3C, almost certainly owing to the presence of Al in the framework. The $\delta$ −109 p.p.m. resonance probably corresponds to Si(1 Al) sites. A spectrum nearly identical to that of ZSM-39 has recently been reported for the structurally related silicate 'holdstite', which suggests that Al was present in that case as well.[6]

The c.p.m.a.s. $^{13}$C n.m.r. spectrum of the dodecasil-3C sample shows that a number of organic species that were present in the synthesis mixture have been occluded. Resonances corresponding to the tetramethylammonium cation, a methoxy group bonded to silicon, methanol, and trimethylamine were found. The Si(1 OMe) moiety is also visible at $\delta$ −103.8 p.p.m. in the $^{29}$Si n.m.r. spectrum. The presence of these residual methoxy groups bonded to the silicate network, absent for the dodecasil-1H sample, shows that not all silicate rings are closed in this dodecasil-3C. Trimethylamine does not appear to be a template as ideal for the dodecasil-3C structure as is 1-aminoadamantane for the dodecasil-1H.

In summary, we have reported the first solid-state n.m.r. spectra of two clathrasils, dodecasil-1H and dodecasil-3C. The c.p.m.a.s. $^{29}$Si n.m.r. spectra allow the assignment of the resonances to the crystallographically distinct $Si(OSi)_4$ sites. The narrow $^{29}$Si resonances found for the dodecasil-1H sample, revealing a well-crystallized structure, together with the $^{13}$C spectrum that indicates the occluded 1-aminoadamantane to be intact, show that this organic additive is an ideal template for this clathrasil.

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