

Long- and Short-Range Constraints for the Structure Determination of Layered Silicates with Stacking Disorder

Sylvian Cadars,^{*,§} Mathieu Allix,[§] Darren H. Brouwer,[‡] Ramzy Shayib,[†] Matthew Suchomel,[#] Mounesha N. Garaga,[§] Aydar Rakhmatullin,[§] Allen W. Burton,[⊥] Stacey I. Zones,[⊥] Dominique Massiot,[§] and Bradley F. Chmelka[†]

[§]CEMHTI CNRS UPR3079, Université d'Orléans, 1D, avenue de la recherche-scientifique, 45071 Orléans cedex 2, France [‡]Department of Chemistry, Redeemer University College, Ancaster, Ontario, Canada, L9K 1J4

[†]Department of Chemical Engineering, University of California, Santa Barbara, California 93106 United States

[#]Argonne National Laboratory, Advanced Photon Source, Argonne, Illinois 60439, United States

¹ChevronTexaco Energy Research and Technology Center, Richmond, California 94802-0626, United States

Supporting Information



ABSTRACT: Layered silicates have important applications as host materials, supports for catalysis, and zeolite precursors. However, their local structures are often challenging to establish due to disorder of the sheet assemblies. We present a new protocol that combines long- and short-range structural constraints from diffraction and solid-state NMR techniques, respectively, to determine the molecular structure of layered silicates in the presence of various extents of stacking disorder. Solidstate ²⁹Si NMR data are largely insensitive to the incomplete extent of three-dimensional (3D) crystallinity that limits the interpretation of diffraction data alone to the identification of possible unit cells and space groups. State-of-the-art NMR crystallography techniques consequently provide a simplified view of materials from which candidate framework structures can be built and evaluated based on local structural constraints, including interatomic distances, Si site numbers and multiplicities, and Si-O-Si connectivities, and refined using density functional theory. This protocol was applied to a new layered silicate material named CLS-1, of composition [Si₅O₁₁H][C₉N₂H₁₅]·1.9(H₂O), synthesized by using a fluoride-based protocol and cationic alkylaminopyridinium as a structure-directing agent (SDA). Despite the intrinsic complexity and partial ordering of the intersheet arrangements and organic-inorganic interactions, this led to the identification of a single space group that is compatible with both NMR and diffraction data, from which the silicate framework structure could be established,. The remarkable similarities between the layered framework structures of CLS-1, HUS-2 (Tsunoji et al. J. Mater. Chem. 2012, 22, 13682), and another layered silicate material with a radically different morphology and extent of stacking order and interlayer dynamics, established by using a similar approach (Brouwer et al. J. Am. Chem. Soc. 2013, 135, 5641), point to the remarkable robustness of this previously unknown silicate framework type.

1. INTRODUCTION

Layered silicate materials or phyllosilicates, either synthetic or of mineral origins, have received much attention in the past because of their high capacities for ion exchange and a large range of applications as adsorbents or catalytic supports, for example. They consist of SiO_4 tetrahedra connected to form two-dimensional (2D) frameworks, with cations and often water molecules in the interlayer spaces. Sodium or magnesium cations are typically intercalated in mineral phyllosilicates, and these can generally be replaced by ion exchange with H^+ , other cations, or cationic organic molecules, such as relatively large quaternary ammonium molecules. Alternatively, layered

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silicates with organic molecules directly incorporated in the interlayer spacing can be synthesized in a single step.^{1–3} Furthermore, the stabilities of these materials can be improved by building interlayer pillars in the form of silsesquioxanes that cross-link to Q³ (i.e., $(SiO)_3Si-OH$ or $(SiO)_3Si-O^-)$ moieties of adjacent layers.^{4,5} Such pillars can in addition incorporate functions leading to catalytic activities or photoresponsive functionalities, for example.⁶ Layered silicates are also important as precursors for the formation of zeolites by conversion (generally by calcination) of their 2D frameworks into structurally related extended three-dimensional (3D) solids.^{7–15} To understand in detail the mechanisms that occur during such transformations, it is crucial to be able to characterize at the molecular level the framework structures of both the final 3D zeolite and the initial 2D layered precursor.

Despite generally high degrees of molecular order in their layered frameworks, determination of the structure of layered silicates is a notoriously difficult problem, which only in a few cases has been solved. These include for example makatite Na₂Si₄O₈(OH)₂·4(H₂O),¹⁶ kanemite NaHSi₂O₅·3H₂O,¹⁷ silinaite NaLiSi₂O₅·2(H₂O),¹⁸ AMH-3,¹⁹ octosilicate, also known as ilerite or RUB-18,^{20,21} [Si₁₂O₂₄(OH)₄][C₆H₅CH₂N(CH₃)₃]₄ RUB-51,²² and very recently yegorovite $Na_4Si_4O_8(OH)_4$; 7(H₂O)²³ and $[Si_{20}O_{40}(OH)_4][HOCH_2CH_2N(CH_3)_3]_4$. 1.03(H₂O) HUS-2.¹⁴ A common factor in all of these systems was the high degree of crystallinity and low degree (if any) of stacking disorder, permitting the collection of high quality Xray diffraction (XRD) data, even in some cases on single crystals. Many phyllosilicate structures, such as that of magadiite $NaSi_7O_{13}(OH)_3 \cdot 4(H_2O)$ or kenyaite $Na_2Si_{22}O_{41}(OH)_8 \cdot 6(H_2O)$, remain unknown despite extensive studies combining diffraction with other techniques.^{24–29} This is in part because single crystals are not readily available, and because disorder in the stacking of the layers or anisotropic distributions of particles that are often present in these systems complicate the analyses of reflection intensities in powder XRD patterns. Thus, although powder XRD generally remains of considerable use, as it provides in particular precise measurements of the basal spacing (i.e., mean distance between adjacent layers), conventional structure-refinement protocols often fail. While in favorable cases the structure of some layered silicates can be determined based on the analogy with a known 3D framework structure^{2,3} (such as the structure formed upon topotactic transformation, for example^{10,13,30}), the situation is significantly more problematic when no such analogy exists or cannot be readily established.

Solid-state nuclear magnetic resonance (NMR) spectroscopy offers attractive potentialities for the characterization of the compositions and structures of layered inorganic or organic—inorganic materials,^{31,32} including layered silicates, due to its sensitivity to local atomic structures, independent of the existence of a long-range 3D periodicity. Solid-state NMR can be used in particular to determine the nature, number, and relative amounts of inequivalent silicon atom sites in a silicate framework.³³ In addition, a handful of molecular-scale interactions may be exploited to shed light onto molecularly ordered silicate structures. The ²⁹Si chemical shift anisotropy (CSA),³⁴ ¹⁷O quadrupolar,^{35–39} and indirect spin–spin coupling interactions (e.g., two-bond ²J(²⁹Si–O–²⁹Si) scalar couplings between two ²⁹Si nuclei connected via a bridging oxygen atom^{1,40–44}) reflect the local composition and bonding geometry around Si and/or O atoms. ¹H–²⁹Si dipolar couplings^{45–51} characteristic of Si–H distances are used to

probe organic–inorganic interactions or establish the existence of hydrogen bonds. 17,29,45,46,49,52 Finally, $^{29}\mathrm{Si}-^{29}\mathrm{Si}$ dipolar couplings associated with Si–Si distances are exploited in NMR-based determinations of high-silica zeolite structures. $^{53-55}$

Here, we report on a new general protocol for the crystallography of layered silicates with imperfect stacking ordering. This protocol combines complementary information from solid-state NMR on the local compositions and structures of the silicate sheets with information on medium and longrange atomic ordering provided by electron and synchrotron XRD, which is sensitive to and often considerably complicated by disorder of the sheet assemblies. In the case of a new layered silicate material referred to as CLS-1, this protocol exploits variable-temperature XRD and NMR measurements and DFT calculations to identify a representative space group and unit cell from which a unique model structure can be determined. Similarities are observed between the silicate frameworks of the CLS-1 and HUS-2 materials and, more surprisingly, a surfactant-directed layered silicate (SDLS) material with radically different morphology,^{1,53} determined separately by using a similar protocol.⁵⁶ Such insights could not have been obtained by using any of the methods alone. In particular, the key new structural constraints provided by solid-state NMR, and their correlations with scattering and DFT analyses, are expected to represent a general approach for determining the structures of silicates or other framework materials with complicated extents of order and disorder.

2. EXPERIMENTAL SECTION

2.a. Materials Syntheses. The CLS-1 materials are prepared with cationic 1-ethyl-4-dimethylamino-pyridinium as a structure-directing agent (SDA) molecule (see Scheme 1). The iodide form of the SDA

Scheme 1. Structure of 1-Ethyl-4-dimethylaminopyridinium Cation



was synthesized by the ethylation of dimethylaminopyridine using ethyl iodide. The resulting iodide salt was dissolved in H_2O and then exchanged to the OH^- form using AGX-X8 resin (BioRad). The resulting alkaline solution was used in concentrations of 0.5 to 1 M.

CLS-1 samples were synthesized using tetraethoxysilane (TEOS) as the silica precursor. Successful syntheses using SiO₂ in the form of CAB-O-SIL and other sources (including $^{29}\mbox{Si-enriched}\ \mbox{SiO}_2)$ were also achieved, as will be reported separately. Reaction mixtures with SDA/Si molar ratios of 0.5 or 1 were prepared in Teflon cups of Parr 4745 stainless-steel reactors and placed in a fume hood at room temperature for several days to evaporate to near dryness. Water was then re-added to the reaction mixture as necessary to adjust the $H_2O/$ SiO_2 ratio to 1.75 or 3.5. Finally, an appropriate amount of HF (48–52 wt % in H₂O) was added to the reaction mixture to achieve a HF/SDA molar ratio of 0.5, 1, or 2. The mixture was gently mixed to minimize any sample heterogeneity prior to sealing the Parr reactor and heating to 150 °C without stirring for 7 days. The final sample was collected by vacuum filtration and washed with excess distilled water (10×50) mL). The washed sample was subsequently dried at 30 °C for 1 day. Table 1 shows a summary of some of the conditions leading to the formation of the CLS-1 material discussed in this work.

2.b. Materials Characterization. Samples for transmission electron microscopy (TEM) were prepared by crushing the powder in *n*-butanol and depositing the small crystallites in suspension onto a holey carbon film, supported by a copper grid. The electron diffraction

Table 1. Examples of Synthesis Mixtures Leading to the Formation of the CLS-1 Material

sample designation	Si source	SDA/ SiO ₂	${ m H_2O/SiO_2}$	SDA/ HF	comment
Α	TEOS	0.5	3.5	1	
В	TEOS	0.5	3.5	0.5	
С	TEOS	0.5	3.5	1	
D	TEOS	1	3.5	0.5	excess "free" SDA present ^a
E	TEOS	0.5	3.5	2	
F	TEOS	0.5	1.75	1	excess "free" SDA present ^a

^{*a*}As manifested by sharp ¹H NMR signals, in addition to the broad signature of incorporated SDA molecules (data not shown).

(ED) study was carried out with a Philips CM20 electron microscope. Energy-dispersive spectroscopy (EDS) analyses were systematically carried out during the ED study, the CM20 being equipped with an EDAX analyzer.

High-intensity and high-resolution room- and variable-temperature synchrotron X-ray powder diffraction data were recorded on the new 11-BM diffractometer at the Advanced Photon Source (APS), Argonne National Laboratory, Argonne, IL. A $\lambda = 0.412213$ Å wavelength was used over the 0.5–50° 2 θ range with a 0.001° step. The sample was contained in a 0.8 mm capillary. Structural analysis was carried out using the JANA software.⁵⁷

Solid-state NMR experiments were conducted on a 7.0 T AVANCE I 300, a 11.7 T AVANCE II+ 500, and a 17.6 T AVANCE II+ 750 Bruker NMR spectrometer operating at ¹H frequencies of 300.15, 500.23, and 750.12 MHz, respectively, and ²⁹Si frequencies of 59.63, 99.37, and 149.03 MHz, respectively. The ¹H and ¹⁹F NMR spectra were collected at 17.6 T using a 1.3 mm double resonance probehead at the spinning frequency of 64 kHz. The quantitative ¹H MAS spectrum was collected with a recycle delay of 10 s. The ¹⁹F MAS single-pulse experiment was collected with a recycle delay of 5 s and 1024 transients. All one-dimensional (1D) and two-dimensional (2D) ²⁹Si measurements were collected at 7.0 or 11.7 T, using a Bruker double-resonance 4 mm probehead, at natural ²⁹Si abundance (4.7%). The quantitative ²⁹Si single-pulse experiment was collected at 11.7 T at the MAS frequency 12.5 kHz, using SPINAL64 heteronuclear decoupling⁵⁸ at the ¹H nutation frequency of 100 kHz, a recycling delay of 900 s, and 176 transients. The two-dimensional ²⁹Si{²⁹Si} refocused INADEQUATE NMR⁵⁹ spectrum was acquired at 11.7 T at the MAS frequency of 10 kHz with a 4 mm probe, using adiabatic cross-polarization⁶⁰ from 1 H, and a contact time of 4.5 ms. Heteronuclear decoupling was achieved using SPINAL64 at the ¹H nutation frequency of 70 kHz. A (half) spin-echo delay (τ) of 7 ms was used. The indirect double-quantum (DQ) dimension was recorded with 128 t_1 increments using the TPPI procedure,⁶¹ and 512 scans with a recycle delay of 5 s (duration: 91 h). Twodimensional ²⁹Si{²⁹Si} dipolar double quantum (DQ) experiments were conducted at 7.0 T with a 4 mm probe, using symmetry-based⁶² SR26411 recoupling,⁶³ at the MAS frequency of 4.6 kHz, and a ²⁹Si nutation frequency of 29.9 kHz (optimized for maximum recoupling efficiency). Heteronuclear decoupling was achieved using CW decoupling at a ¹H nutation frequency of 90 kHz during the recoupling (i.e., ca. 3 times the ²⁹Si recoupling power to avoid interferences⁶⁴), and SPINAL64 at 50 kHz during acquisition in both dimensions. The number of recoupling supercycles for the DQ excitation and reconversion blocks was incremented from 1 to 13 (from 1.7 to 22.6 ms recoupling before and after t_1). The indirect dimension was collected with 112 t_1 increments using the States procedure,⁶⁵ with 64 scans and a recycle delay of 4.6 s (duration: 9 h per 2D spectrum). All chemical shifts are given relative to (neat) TMS. Other specific experimental details are given in appropriate sections of the text and/or figure captions.

2.b. DFT Calculations. Density functional theory (DFT) calculations with periodic boundary conditions were achieved on a

plane-wave-based approach using the CASTEP code.^{66,67} The electron correlation effects are modeled using the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA).⁶⁸ For geometry optimizations, we employed a planewave cutoff energy of 650 eV and ultrasoft⁶⁹ pseudopotentials described in Supporting Information (Table S1). Convergence thresholds were set to 10^{-5} eV/atom for the total energy, 3×10^{-2} eV/Å for the maximum ionic force, and 10^{-3} Å for the maximum ionic displacement. Nonbonding forces were accounted for by the damped atom-pairwise semiempirical dispersion corrections of Tkatchenko and Scheffler.⁷⁰ Structural models used the C2/c (#15) space group, with a primitive cell of dimensions a = b = 9.314 Å, c = 30.211 Å, $\alpha = \beta = 90.11^{\circ}$, and $\gamma = 132.90^{\circ}$, which were kept fixed during geometry optimizations. A $3 \times 3 \times 1$ Monkhorst–Pack⁷¹ (MP) grid was used to sample the Brillouin zone.

The NMR calculations were performed using the Gauge Including Projector Augmented Wave approach (GIPAW),^{72,73} at the same cutoff energy of 650 eV, which led to calculated ¹H and ²⁹Si NMR shieldings converged within less than 0.1 ppm. Reliable derivation of NMR chemical shifts from the NMR shielding values calculated by DFT was achieved on the basis of the correlation plots between experimental chemical shifts and shieldings calculated for a series of reference crystal systems of known structure. These systems are oxides with four-coordinated Si atoms for ²⁹Si calculations, hydroxide inorganic materials for ¹H calculations, and the α polymorph of testosterone for ¹³C calculations (38 fully assigned ¹³C signals covering the entire ¹³C spectral range⁷⁴). The correlation equations were as follows: $\delta_{iso}(ppm) = -0.922 \sigma_{iso} + 283.39$ for ²⁹Si, $\delta_{iso}(ppm) = -0.926 \sigma_{iso} + 160.94$ for ¹³C, and $\delta_{iso}(ppm) = -0.845 \sigma_{iso} + 26.04$ for ¹H.

3. RESULTS AND DISCUSSION

3.a. Long-Range Molecular Order and Disorder in CLS-1. A novel siliceous (i.e., heteroatom-free) layered material was synthesized following a method introduced by Zones and co-workers, and which has been used to synthesize several siliceous zeolites.75-77 This method relies on the structuredirecting role of fluoride which, through processes that are not yet fully understood, promotes the crystallization of highly ordered molecular sieves in the absence of trivalent heteroatoms (e.g., Al, B) that are often required for the formation of zeolites. 76 Here, appropriate choice of the SDA (see Scheme 1) led to the formation of a new layered material that exhibits a high extent of crystal-like order, as suggested by platelet particle shapes in Figure 1a,b and the electron diffraction pattern in Figure 1c. The flower-like aggregates in Figure 1a are composed of assemblies of well-defined 2D platelets with dimensions of 1 to 30 μ m in the plane and of the order of 50 to 100 nm in thickness. Medium to long-range molecular order (typically a few hundreds of nanometers) within individual particles is confirmed by the electron diffraction pattern (Figure 1c), which was obtained by focusing the electron beam on an isolated particle oriented parallel to the substrate. (It was not possible to study particles lying along different orientations, due to their platelet shapes.) This gives important information on the in-plane unit cell parameters. Specifically, the two *a* and *b* basis plane cell parameters can be determined as 7.4 \pm 0.1 Å and 17.1 \pm 0.2 Å, the in-plane γ angle appears to be 90.0° ($\pm 0.1^{\circ}$), and the extinction condition (hk0, h + k = 2n + 1) indicates the presence of a *n* glide perpendicular to the *c* axis. No indication of structural disorder, which would be manifested by streaks, is observed within the basis plane, confirming the high degree of long-range molecular order within the layers.

In contrast, the 3D structure of the CLS-1 material is substantially more complicated. A synchrotron powder XRD pattern, presented in Figure 2a, shows an intense 00*l* peak at



Figure 1. (a, b) Scanning electron microscopy images of CLS-1 layered silicate material. The planar shape of the particles is consistent with a layered structure. (c) [001] Electron diffraction pattern of a single particle.

low angle $(2\theta = 1.57^{\circ})$ typical of long-range ordering of the layers, while the large number of sharp reflections observed at wider angles confirms the high degree of long-range molecular order. An autoindexing analysis was performed to determine the cell parameters, which led to a common solution with acceptable reliability factors using both Dicvol⁷⁸ and Treor⁷⁹ softwares. The obtained unit cell was orthorhombic with a =7.46 Å; b = 17.12 Å, and c = 15.11 Å, which is in good agreement with the electron diffraction results. A Lebail⁸⁰ refinement (profile fitting integrating information on the unit cell size shape, and symmetry, independent of its content) was then undertaken to refine the unit cell parameters and observe the reflection conditions. In addition to the *hk*0, h + k = 2ncondition determined by electron diffraction, a 0kl, k = 2n extra condition appears, leading to a set of possible space groups including *Pbmn* (no. 53) or *Pb2n* (no. 30) if an orthorhombic

system is considered, or C2/c (no. 15) for a monoclinic setting. The refined unit cell parameters are indicated in the first three rows of Table 1. The indexations corresponding to these solutions are shown in Supporting Information, Figure S2.

The quality of the synchrotron scattering data (manifesting dramatic improvement in resolution, compared to conventional XRD results, not shown) points to the high degree of longrange molecular order in these materials, but it also reveals several complications upon closer examination. Despite a reasonable overall agreement between the predicted and experimental positions of the reflections (for this type of materials) and their consistency with the electron diffraction data, a few reflections remain that could not be properly indexed in our model. This could point to the existence of small amounts of crystalline impurities which have not yet been identified. Furthermore, some reflections, in particular the (11l) reflections at $2\theta = 3.8^{\circ}$ (112) and 4.7° (114), are broadened, with complicated shapes that suggest possible polycrystallinity. These reflections clearly involve the interlayer arrangement, indicating despite its high degrees of long-range molecular order within the layers, that the CLS-1 material cannot be simply described by a unique and atomically periodic stacking of the layers. Interestingly, the same (111) reflections show major differences for different synthesis mixtures (Table 1), as highlighted in Figure 2b for CLS-1 samples B and C. This indicates that polymorphs with slightly distinct unit cell parameters could coexist in various relative amounts in the CLS-1 samples.

Previous works on layered materials have pointed to an important paradox that can be exploited here to refine the indexing of the synchrotron XRD data collected on the CLS-1 materials, despite the complications described above. In cases where the extent of stacking disorder is large or complete, i.e., when there is complete rotational and translational disorder of adjacent layers (also referred to as turbostratic disorder), a large part of the diffraction peaks vanish from the diffraction pattern. These include (with the c axis representing the direction perpendicular to the layers) all (0kl), (h0l), and (hkl) reflections with *h*, *k*, and $l \neq 0$, which necessitate long-range atomic periodicity both within and between the planes. Remaining reflections are the (hk0) reflections related to long-range molecular order within individual sheets, and (00*l*) reflections associated with the basal spacing (interlayer distance), which are in this case independent of the existence of molecular order within the sheets. Examples of such situations include in particular surfactant-directed layered materials, where layers with short- or long-range molecular order are separated by bilayers of amphiphilic molecules with long and flexible alkyl chains, resulting in large extents of interlayer disorder.^{1–3,53,56} This made it possible, for example, to index diffraction peaks in layered systems based on known three-dimensional analogue structures^{2,3} or to determine the inplane unit-cell parameters in the absence of such known 3D analogue structure.⁵⁶ In the case of the comparatively highly ordered CLS-1 material, we hypothesized that increasing the interlayer disorder by increasing temperature could paradoxically help peak indexation, which is complicated at room temperature by the potential presence of unknown crystalline impurities and a small extent of polymorphism and/or interlayer disorder.

Variable-temperature synchrotron powder diffraction experiments reveal temperature-induced distortions and disordering of the CLS-1 unit cell that are compatible with only one of the



Figure 2. (a) Powder synchrotron X-ray diffraction pattern (red circles) of layered silicate CLS-1, sample B, collected at room temperature. Below is the indexation using two coexisting phases with the same C2/c space group (I: a = 7.4430(3), b = 17.0836(4), c = 30.150(1), and $\beta = 91.134(3)$; II: a = 7.4772(5), b = 17.120(2), c = 30.153(2), and $\beta = 90.317(6)$). The corresponding Lebail fit (with arbitrary peak intensities) is shown in as a solid black line. (b, c) Magnification of a region of interest of the synchrotron XRD patterns of CLS-1 samples B and C and corresponding Lebail fits (in black). The (111) reflection regions where the coexistence of two distinct polymorphs whose relative amounts vary between samples are highlighted with dotted blue lines in b and c.



Figure 3. Variable-temperature (a) synchrotron XRD and (b) solid-state 29 Si CP-MAS NMR experiments collected on CLS-1, sample C. (b) 29 Si CP-MAS spectra were collected at 5 kHz MAS, with a CP contact time of 4 ms. The temperature inside the rotor was monitored by using the 207 Pb NMR signal of inert PbNO₃ powder mixed with the sample. The spectrum at the bottom was collected after cooling the sample back to room temperature.

identified candidate space groups. Specifically, synchrotron XRD diffraction data collected between 20 °C and 150 °C and shown in Figure 3a show a first transition between 60 °C and 70 °C (highlighted in red in Figure 3a), with a clear splitting of the (11*l*) reflections, whose complicated shapes are discussed

above. It was possible to explain such modifications by considering that the material is composed of two distinct phases with slightly distinct unit cell parameters (i.e., two polymorphs), one of which undergoes a substantial modification of one unit cell angle when the temperature increases

		unit cell parameters						
space group (number)	T (°C)	a (Å)	b (Å)	c (Å)	α (deg)	β (deg)	γ (deg)	
<i>Pbmn</i> (no. 53)	20	17.08	7.442	15.07	90 ^a	90 ^a	90 ^a	
<i>Pb2n</i> (no. 30)	20	17.08	7.442	15.07	90 ^{<i>a</i>}	90 ^a	90 ^{<i>a</i>}	
C2/c (no. 15)	20	17.08	7.442	30.16	90 ^{<i>a</i>}	90.00	90 ^{<i>a</i>}	
C2/c (no. 15)	20	7.443	17.08	30.15 ^b	90 ^a	91.13 ^b	90 ^{<i>a</i>}	
		7.477	17.12	30.15 ^b		90.32 ^b		
C2/c (no. 15)	90	7.464	17.04	29.90 ^b	90 ^a	90.45 ^b	90 ^{<i>a</i>}	
		7.431	17.12	30.02 ^b		94.08 ^b		
N.A.	150	7.345	17.13	27.74	90 ^c	90 ^c	90 ^c	
^{<i>a</i>} Fixed by space group. ^{<i>b</i>} Coexistence of (at least) two distinct phases. ^{<i>c</i>} Fixed for simplicity.								

Table 2. Candidate Space Groups and Unit Cell Parameters Examined for the New Layered Silicate Material CLS-1 (from samples B and C)

above 70 °C. Among the possible space groups identified above, only one, the C2/c space group, is compatible with such a distortion (the other groups being orthorhombic). Because β is the only free angle in this monoclinic group, the a and bparameters must be as indicated in the fourth row of Table 2, rather than the reverse setting arbitrarily used in the initially suggested indexations (first three rows in Table 2). On this basis, the two new contributions that appear above 70 °C on both sides of the reflection at ca. $2\theta = 4.7^{\circ}$ can be assigned to the (114) and (11 $\overline{4}$) reflections of a phase with a distorted β angle (*a* = 7.431, *b* = 17.12, *c* = 30.02 Å, and β = 94.08°), while the central part of the (114) contribution corresponds to a coexisting phase with a smaller β value (a = 7.464, b = 17.036, c= 29.90 Å, and β = 90.45°). This interpretation is also consistent with the modifications of the (112) reflection at ca. $2\theta = 3.8^{\circ}$ in the same temperature range. The indexation and corresponding Lebail Fit of the synchrotron XRD data collected for CLS-1 sample B at 90 °C (Supporting Information, Figure S3) show that the entire pattern at this temperature is reasonably well accounted for by this two-phase model.

Above 110 $^{\circ}$ C, the same (11*l*) reflections completely disappear from the diffraction pattern. Some others, such as the (00l) and the (0kl), shift and broaden, while the (0k0)reflections remain sharp and intense, with their position unaffected. Such modifications may be fully explained by a complete disordering of the material parallel to the *a* axis (which can also be interpreted as large variations of β angles), concomitant with a reduction of the *c* parameter and thus of the interlayer space. The essentially unchanged position of (020) reflection, in contrast, indicates that the molecular order within the layers remains unaffected and that this disordering only concerns the stacking of the layers. We note that (h00)reflections are more difficult to analyze because they largely overlap with other reflections throughout the entire diffraction pattern and are correlated with the β angle, which varies as a function of temperature.

The room-temperature synchrotron data were then reexamined on the basis of these findings, to obtain a significantly improved indexation of the diffraction peaks. Figure 2b,c shows magnifications of the room-temperature synchrotron XRD patterns (red circles) collected for CLS-1 samples B and C, respectively. As for the data collected at 90 °C, two phases with slightly distinct cell parameters were found to coexist at room temperature (phase I with a = 7.443, b = 17.084, c = 30.15 Å, and $\beta = 91.13^{\circ}$, and phase II with a = 7.477, b = 17.12, c =30.15, and $\beta = 90.32$). This consideration leads to a correct Lebail fit of the (11*l*) reflections for the different samples (B and C) having different polymorph ratios. The corresponding Lebail fit and difference between the experiment and the fit (shown in black in Figure 2b and 2c) point to a good agreement with the experimental data for both samples, their different signatures being due to differences in the relative amounts of the two phases present in each sample (which cannot be estimated from Lebail fits).

In marked contrast with diffraction data, solid-state ²⁹Si NMR experiments collected in the same temperature range show very little modifications, reflecting the essentially local character of this spectroscopy. Figure 3b shows ²⁹Si{¹H} CP-MAS NMR experiments collected on CLS-1 sample C between 46 °C and 118 °C and then back to room temperature (at the bottom) after cooling the sample. Below ca. 70 °C the spectra show five main peaks at -97.5, -98.5, -106.0, -111.2, and -117.2 ppm, which are labeled (from left to right) sites 1, 2, 3, 4, and 5. The positions of overlapping sites ²⁹Si sites 1 and 2, suggest that they correspond to ²⁹Si Q³ [i.e., (SiO)₃SiO⁻ or (SiO)₃SiOH] environments, whereas sites 3, 4, and 5 are fully condensed ²⁹Si Q⁴ [i.e., Si(OSi)₄)] environments.³³ (This was confirmed by the observation at slow MAS frequencies of spinning sidebands for ²⁹Si peaks 1 and 2 but not for other peaks, consistent with much stronger 29Si chemical shift anisotropy associated with the more asymmetric environment of Q^3 sites). With increasing temperature, peak positions change slightly, with a stronger overlap of peaks 1 and 2 in particular, but the spectrum nevertheless remains essentially the same. Furthermore, the spectrum collected after cooling the sample is virtually identical to the initial room-temperature spectrum. This indicates that the molecular structure within the sheets remains intact up to 120 °C, consistent with the unaffected (0k0) reflection in variable-temperature diffraction data. Thus, while diffraction data indicate major modifications of the interlayer ordering at medium to long-range scales as a function of temperature, solid-state ²⁹Si NMR provides a local, essentially intralayer local point of view that is largely unaffected by interlayer disorder. This important distinction is the key to the use of solid-state NMR for solving the structures of molecularly ordered materials with incomplete (or even lacking⁵⁶) three-dimensional crystallinity.

3.b. Local Composition and Structure. In contrast with diffraction techniques, every single nucleus contributes to solid-state NMR spectra, independent of the existence of molecular order. The position of the corresponding signal on the spectrum is in most cases determined by the local (less than 1 nm) environment. Solid-state ¹H NMR can be used to probe the organic SDA molecule (see Scheme 1 above) and its presence in the interlayer space of the CLS-1 material.

Specifically, the fast MAS ¹H NMR spectrum of the CLS-1 (sample B) shown in Figure 4a shows well-resolved peaks that can be assigned to aromatic (at 8.2 and 6.9 ppm), NCH₂ (at 4.5 ppm), NCH₃ (at 2.6 ppm), and CH₂CH₃ (at 1.8 ppm) protons of the SDA molecule. Another peak at 16.2 ppm can be assigned by analogy to other layered silicates to silanol ¹H



Figure 4. Solid-state NMR spectra of the layered silicate CLS-1. (a) Quantitative ¹H MAS NMR spectrum of sample B (in black), along with the best fit (in red) and corresponding spectral deconvolution into SDA (in blue) and surface and/or intercalated SiOH and/or water moieties (in yellow). (b) Single-pulse ²⁹Si MAS NMR spectrum of sample A, acquired at 11.7 T at a MAS frequency of 10 kHz, with a recycle delay of 900 s. (c) 2D refocused INADEQUATE ²⁹Si{²⁹Si} spectrum of sample A, collected at 11.7 T, at a MAS frequency of 10 kHz. Cross peaks indicate through-bond ²⁹Si-O-²⁹Si connectivities. Lowest contour levels are $\pm 12.5\%$ of the maximum intensity, with negative contours being shown in red and positive in black. The gray region indicates artifacts at the carrier frequency. (d) Dipolar-couplingmediated ²⁹Si double quantum (DQ) spectrum of sample B, collected at 7.0 T, at a spinning frequency of 4.6 kHz. Cross-peaks indicate in this case spatial Si-Si proximities. The mixing times (i.e., so-called DQ excitation and reconversion blocks) were set to 7.0 ms, a duration that was optimized to selectively probe short $^{29}\text{Si}{-}^{29}\text{Si}$ distances (ca. 3.0 Å) associated with ²⁹Si-O-²⁹Si connectivities.

involved in hydrogen bonds between Si-O groups (Si-O-H… O-Si protons) located either in two adjacent layers^{29,45,46} or within the same layer.^{17,52} This observation points in either case to strong connectivities between adjacent Q^3 sites that might contribute to the high degree of molecular order in this material. Quantification of the relative amounts of each ¹H moieties in this spectrum can be obtained from spectral deconvolution (using the DMfit program⁸¹). This leads to relative areas of the SDA proton signals in reasonable agreement with their multiplicities. Another broad ¹H signal at ca. 6 ppm is attributed to intercalated and/or surface water molecules, with intensity indicating a population of ca. 1.8 (± 0.5) water molecules per SDA molecule (although the broadening and fast dephasing of this signal makes it difficult to quantify accurately). Most importantly, the quantifications of ¹H NMR signals clearly establish that there is one Si-O-H… O-Si proton per SDA molecule in the structure to compensate in part for the negative charges of ²⁹Si Q³ [i.e., (SiO)₃Si-O⁻ and/or (SiO)₃Si-OH)] moieties invariably present in layered silicates.

The amounts of such Q³ entities were measured by solidstate ²⁹Si NMR and found consistent with this hypothesis. The ²⁹Si single-pulse spectrum of the CLS-1 layered silicate material, sample A, is shown in Figure 4b, with the five main peaks at -97.6, -98.9, -106.0, -111.0, and -117.3 ppm labeled as in Figure 3b. The relative populations of these sites are directly obtained from this quantitative spectrum by peak integration. Partially, overlapping Q³ sites ²⁹Si sites 1 and 2 are found to account for 2/5 of the overall ²⁹Si signal, while Q⁴ sites 3, 4, and 5 each correspond to 1/5, indicating that all of these sites are equally populated. In light of the quantitative ¹H NMR data, which indicate a 1:1 ratio between the number of SDA molecules and of Si-O-H…O-Si protons, ²⁹Si NMR results suggest that the two negative charges associated with each pair of Q^3 (SiO)₃Si-O⁻ moieties are balanced by one Si-O-H··· O-Si proton and one SDA molecule. Combined with ¹H NMR data, this leads to the composition $[Si_5O_{11}H][C_9N_2H_{15}]$. $1.8(H_2O).$

This sample composition, derived from quantitative NMR data, is confirmed by thermogravimetric analyses (TGA) (see Supporting Information, Figure S4). A first mass loss (of ca. 7%) between 50 °C and 180 °C is attributed to the sample dehydration. A major mass loss between 250 °C and 400 °C is then assigned to the degradation of the SDA, which is followed at higher temperatures by a gradual elimination of the remaining degradation products, concomitant with water release due to condensation of the basic Si₅O₁₁H units of the layered framework into dense SiO₂. These data are used to calculate a 1:1 ratio (with less than 10% error) between Si₅O₁₁H units and the SDA molecule, and 1.9 H₂O molecules per SDA molecule, which is in excellent agreement with the quantitative ¹H NMR data.

A ¹⁹F spectrum (Supporting Information, Figure S5) shows only very small amounts of residual ${\rm SiF_6}^{2-}$ and other unidentified fluorine-containing impurities, which indicates that fluorine atoms do not play a charge-compensating role in CLS-1, in contrast with three-dimensional zeolites synthesized with the same protocol.⁷⁷ This is because ordered negatively charged Q³ sites compensating for the positive charge of the structure-directing agent are absent in fully condensed three-dimensional zeolitic frameworks.

In addition to the nature and relative population of each inequivalent ²⁹Si site in the silicate framework, ²⁹Si solid-state

NMR can be used to probe the existence of through-bond Si– O–Si connectivities. This is achieved with so-called doublequantum single-quantum (DQ-SQ) experiments mediated through the scalar (*J*) couplings (or "INADEQUATE"-type experiments^{59,82–84}), specifically here between ²⁹Si nuclei connected via a Si–O–Si linkages, abbreviated as ²*J*(²⁹Si– O–²⁹Si) couplings.^{40–42,44,53,54,85–87} Figure 4c shows the twodimensional map obtained from such an experiment collected on CLS-1 material, sample A. Pairs of cross-peaks highlighted with green lines reveal that Si–O–Si connectivities exist among pairs 1-5, 2-4, 2-5, 3-4, 3-5, and 4-5, and presumably pair 1-2 (smaller-intensity signal at –197.2 and –99.2 ppm in vertical and horizontal dimensions, respectively).

Similar DQ-SQ correlation experiments that probe spatial ²⁹Si-²⁹Si proximities rather than through-bond connectivities provide complementary information with generally higher signal-to-noise. Specifically, we used here a sequence of RF pulses referred to as SR26411 dipolar DQ-SQ recoupling,63 which is one of many methods that use dipolar recoupling to reintroduce the homonuclear dipole-dipole couplings to probe spatial proximities and/or measure internuclear distances in solids.^{62,88} Figure 4d shows the 2D correlation map obtained for sample B with this experiment, in conditions optimized to yield intense cross-peaks for the short Si-Si distances of ca. 3 Å between connected 29 Si $-O-{}^{29}$ Si pairs and weak or negligible cross-peaks for the longer distances associated with nonconnected pairs.⁵⁴ This spectrum confirms that a Si–O–Si connectivity exists between sites 1 and 2. It also establishes that ²⁹Si sites 1 and 3 are very close to each other and form a Si(1)-O-Si(3) connection, only with a ²*J*(²⁹Si- $O-^{29}Si$) coupling too small to yield detectable cross-peak intensity in the J-mediated DQ-SQ spectrum of Figure 4c. This leaves missing connectivities for Si sites 3 and 4, which, as Q⁴ species, should have four connected Si neighbors. The absence of signal intensity on the spectrum diagonal at the expected positions of 3-3 and 4-4 cross-peaks in Figure 4d rules out the possibility that each is coupled to an identical site. Indeed, whereas diagonal cross-peaks would not be visible in the *I*-mediated experiment because the effect of the J coupling vanishes between two sites of identical chemical shifts, they would be visible in the dipolar-mediated experiment if such connectivities existed (see for example ref 54). Instead, both through-space and through-bond spectra show the most intense signal intensities for cross-peaks associated with ²⁹Si-²⁹Si pair 3-4, which indicates that Si site 3 is connected to two distinct Si sites 4, and Si site 4 is connected to two distinct Si sites 3. This reveals the existence in the layered framework structure of fourmembered rings formed by an alternation of sites 3 and 4 (3-4-3-4). This combination of through-bond and through-space ²⁹Si DQ NMR experiments thus provides the complete set of Si-O-Si connectivities characteristic of the topology of CLS-1 material's layered silicate framework.

3.c. Structure Solution Based on Short-Range Si–Si Distance Constraints. Solid-state ²⁹Si NMR measurements can furthermore be exploited to generate atom by atom and evaluate candidate silicate framework structures on the basis of multiple Si–Si distance constraints.^{54,55} This strategy, initially developed for high-silica zeolites, is of considerable interest for layered silicates because it is based on the strictly local point of view of dipole–dipole interactions between ²⁹Si nuclei. Specifically, the three-dimensional structures of zeolites Sigma-2 (SGT framework), ITQ-4 (IFR framework), and ferrierite (FER framework) could be accurately described by considering only Si–Si distances smaller than 0.8 nm.^{54,55,89} This means that, in the case of layered silicates, this analysis will be essentially restricted to intrasheet information and thus largely insensitive to the stacking disorder, in contrast with diffraction data.

The structure-determination algorithm (described in more detail in ref 55) uses the unit cell parameters and space groups obtained by diffraction techniques (using the positions of the reflections and possible extinctions pointing to symmetry elements), and a set of 2D ²⁹Si DQ-SQ dipolar recoupling spectra (as in Figure 4d) collected with various recoupling durations as inputs. The longer the recoupling duration (called DQ excitation and reconversion times), the longer the distances probed, as illustrated in the Figure 5a spectrum



Figure 5. (a) Dipolar-coupling-mediated ²⁹Si{²⁹Si} double quantum (DQ) spectrum of sample B (same as in Figure 3d), collected at 7.0 T, at a spinning frequency of 4.6 kHz. The mixing times were set to 20.9 ms to probe both short ²⁹Si–²⁹Si distances associated with ²⁹Si– O^{-29} Si connectivities and longer-range distances, indicated in red. (b) Experimental DQ curves (black squares) obtained by 2D deconvolution of the corresponding cross-peaks in a series of dipolar-mediated DQ-SQ experiments collected with mixing times ranging from 3.5 to 22.6 ms. The red curves correspond to simulations obtained with the model structure shown in part c, which is consistent with all available ²⁹Si NMR and diffraction data.

collected with a mixing time of 20.9 ms. This spectrum shows a number of additional cross-peaks (indicated in red) as compared to the spectrum of Figure 4d (collected with a shorter mixing time of 7.0 ms), which point to comparatively longer-range spatial proximities between pairs of ²⁹Si nuclei that are not connected by bridging oxygen atoms. The cross-peak intensities obtained from 2D deconvolution of the spectra are

reported as functions of the DQ mixing time in Figure 5b (black squares). These so-called "double-quantum (DQ) buildup curves", along with the unit cell parameters and possible space groups determined from power XRD data, were used as input to the structure-determination algorithm developed for solving the crystal structures of zeolites from solid-state NMR data.⁵⁵ The strategy essentially involves an automated modelbuilding algorithm which, given a space group, searches for candidate structural models whose calculated DQ build-up curves are consistent with the experimentally observed data.

If the space group is compatible with the ensemble of available local structural constraints from ²⁹Si NMR, a set of candidate or ideally a unique framework structure(s) (described only by their Si atom positions at this point) is obtained. This was not the case for possible space groups Pbmn (no. 53) or Pb2n (no. 30), which turn out to be incompatible with a layered silicate framework structure given the Si-O-Si connectivities in particular. Among the space groups identified as possible space groups on the basis of electron and synchrotron diffraction data, only C2/c (no. 15) appears to be compatible with both long- and short-range constraints provided by diffraction and ²⁹Si NMR data, respectively. In this case the algorithm ultimately retains a total of six possible candidate silicate framework structures among all existing possibilities. One example of these structures is shown in Figure 5c, with Si sites 1, 2, 3, 4, and 5 shown in yellow, orange, red, green, and blue, respectively, and gray sticks indicating Si-O-Si connectivities. Among these six structures, three pairs of structures are exactly identical but for the inversion of Si site labels (1, 2) and (3, 4), which leads to the exact same set of connectivities. (The Si sites are indeed labeled by decreasing experimental ²⁹Si chemical shift, while chemical shift information is not taken into account at this point of the procedure.) This leaves only three possible structures, which, although close because they include in particular the same structural elements (four-, five-, and six-membered rings with identical sequences of Si sites), are not strictly identical.

Because the structure-solution algorithm only considers tetrahedral sites, O and H atoms and the organic SDA molecule must be placed separately in the model. Figure S6 in Supporting Information shows the superposition of three candidate framework structures along with superpositions of fragments of some these framework structures aligned to allow direct comparisons (Figure S6c). These structures, which include O and H atoms in addition to the Si atoms positioned by the algorithm, were obtained as follows. Bridging oxygen atoms were first inserted midway between connected Si atoms, and nonbridging O atoms were placed to form crude tetrahedral SiO4 moieties. All atomic positions in the silicate framework were then relaxed using an empirical distance-leastsquares (DLS) approach⁹⁰ using expected Si-O, O-O, and Si-Si distances from known zeolite crystal structures. As established above from quantitative ¹H NMR and TGA experiments, global neutrality is obtained by balancing the negative charges of the two Q^3 sites in the basic Si₅O₁₁²⁻ unit with one SDA molecule and one proton, forming a strong Si-O-H…O-Si linkage. There used to be a debate to establish whether Si-O-H…O-Si moieties detected in various layered silicates (kanemite, magadiite, octosilicate RUB-18, kenyaite) by means ¹H peaks at high chemical shifts (of the order of 16 ppm, as for CLS-1) corresponded to inter-29,45,46 or intrasheet^{17,52} bridges. In CLS-1, our models indicate that the distance between adjacent layers is too large to present intersheet bridges. On the other hand, H atoms could be placed between a pair of adjacent, but not connected, sites Si(1) and Si(2) (as illustrated in Supporting Information, Figure S6d), where the small distance between the associated nonbridging oxygen atoms (between 2.57 and 3.11 Å) would be compatible with the high ¹H chemical shift values measured here. H atoms were thus systematically placed midway between these two O atoms to (hopefully) form Si(1)–O···H–O–Si(2) or Si(1)–O–H···O–Si(2) moieties upon subsequent geometry optimizations.

The ultimate and most critical step consists of the incorporation in the model of the SDA molecules (one per unit cell, the other seven being directly obtained by symmetry). Water molecules (1.9 per SDA molecule, as established by ¹H NMR and TGA) are omitted for simplicity in the models. For each candidate framework, various initial positions could be found that avoided overlap with both the silicate framework and adjacent SDA molecules (symmetric and periodic images). All of these structures were then relaxed with quantum chemical calculations at the planewave-based density functional level of theory (DFT) with pseudopotentials to describe core electrons. This approach describes a full infinite crystal through periodic boundary conditions and may include recently developed semiempirical corrections on dispersive forces, which tend to considerably increase the reliability of DFT calculations for the description of nonbonding interactions.⁷⁰ In contrast with the structure solution protocol based on ²⁹Si NMR data, which performs a systematic search across all inorganic framework structures that could possibly exist, only a finite set of initial SDA positions and orientations could be considered among the large ensemble of possibilities. Specifically, we tried to align the main axis of the SDA molecule parallel to either the a, b, or c crystallographic axis and in each case considered several orientations of the pyridine ring, in an attempt to obtain a small (because of computational requirements) but nevertheless representative set of possible SDA orientations.

The structures obtained after geometry optimization (with fixed cell parameters) starting from one of the three distinct framework structures derived from the structure-solution algorithm are shown in Figure 6. The different model structures are labeled from I to VI. Interestingly, the silicate framework is not strongly affected by the position or the orientation of the SDA molecules, as is more obvious from the superposition of all structures shown in Supporting Information, Figure S7. Particularly interesting is the convergence of the three initially distinct candidate framework structures into a single structure after geometry optimization. This indicates that, as far as the inorganic framework is concerned, unique structure determination was achieved despite the intrinsic complexity of this material.

The candidate model structures of CLS-1 can be evaluated on the basis of several numerical parameters, which are reported in Table 3. The first is the total energy as calculated with DFT, which shows significant differences between the six candidate structures, with a single structure, structure **V**, being 1.5 eV (145 kJ mol⁻¹) more stable than any other structure. This structure shows an alignment of the main axis of the SDA molecules (i.e., the N–N direction) parallel the *c* axis, with pyridine rings in the *b*,*c* plane. Adjacent pyridine rings surprisingly do not align to form π – π interactions, whereas these are in principle accounted for by the semiempirical treatment of dispersive forces included in our calculations.⁷⁰



Figure 6. Partial views, in the *b*,*c* plane, of six distinct model structures of CLS-1 with C2/*c* space group and $\beta = 90.28^\circ$, obtained by DFT optimization after incorporation of the SDA molecules at different arbitrary initial positions and orientations in the interlayer space.

Table 3. Numerical Parameters for the Comparisons ofDFT-Optimized Candidate Model Structures of CLS-1

		chemical shift RMSD ^a (ppm)				
structure	$E_{\rm final}~({\rm eV})$	²⁹ Si	$^{1}\mathrm{H}$	¹³ C		
I	-31567.8	1.2	1.4	5.9		
II	-31567.8	2.5	1.4	5.2		
III	-31569.0	2.1	1.3	7.0		
IV	-31566.7	4.0	1.4	5.7		
v	-31570.5	0.5	1.1	4.8		
VI	-31569.0	2.1	1.3	7.0		

^{*a*}RMSD_{cs} = $((1/N)\sum_{i=1}^{N} [\delta_{calcd}(i) - \delta_{exp}(i)]^2)^{1/2}$, where $\delta_{exp}(i)$ are the experimental chemical shifts of ²⁹Si, ¹³C, or ¹H site *i*, $\delta_{calcd}(i)$ are the chemical shifts calculated with plane-wave-based DFT and referenced as detailed in Experimental Section.

Other opportunities for the evaluation of these structures are offered by the comparison of experimental ²⁹Si, ¹H, and ¹³C NMR chemical shifts with values calculated on all optimized structures by DFT, ^{91,92} using the gauge-including projector-augmented wave (GIPAW) approach.⁷² The results are shown in Figure 6 in the form of correlation plots between experimental and calculated data. The corresponding agreement factors are estimated in the form of root-mean-square deviations (RMSD), which are reported in Table 3 (χ^2 values, reported in Supporting Information Table S3, show similar trends). These results support the conclusions drawn based on DFT total energies. Calculated ¹³C data allow us to reject

structures III and VI (RMSD of the order of 7 ppm as compared to values of 5.9 ppm or lower for other structures) due to a higher-energy conformation of the SDA ethyl group. The lowest deviation between experimental and calculated data is obtained for structure V (RMSD of 4.8 ppm as compared to 5.2 or higher for the other structures), which, interestingly, is also the lowest-energy structure. Nevertheless, the overall agreement between calculated and experimental ¹³C NMR data remains rather poor as compared to what can be expected for well-defined crystalline structure (see the example of testosterone in Supporting Information, Figure 1c), which suggests that the intermolecular interactions representative of the packing of SDA molecules within the interlayer space have not been entirely captured (possibly in part because water molecules are omitted in these models). Nevertheless, calculations of ¹H chemical shifts fully support the existence of intralayer Si(1) - O - H - O - Si(2) or Si(1) - O - H - O - Si(2)linkages, with predicted ¹H chemical shifts between 12.7 and 14.2 ppm for the different candidate structures, not far from the experimental value of 16 ppm. Furthermore, and most importantly, we find again that structure V (green " ∇ " symbols in Figure 7), the most stable structure according to energy calculations, gives the best agreement between experimental and calculated chemical shifts for both ¹H and ²⁹Si (RMSD of 0.5 and 1.1 ppm, respectively). This suggests that this model is most representative of the local interactions between the silicate framework and SDA molecules in the interlayer space. Furthermore, the quality of DFT predictions of ¹H and even more so ²⁹Si NMR parameters for this structure fully confirm that the silicate framework structure found by the structure-solution algorithm and then refined by DFT is indeed the correct one.

Among the complications of the CLS-1 material at length scales longer than probed by solid-state NMR is the coexistence at room temperature of two distinct phases with slightly distinct unit cell parameters. (There could actually be a distribution of slightly distinct structures such that even the coexistence of two polymorphs may still be an oversimplification.) The full approach discussed above was thus repeated for the second phase with slightly different c (30.14 Å) and β (91.14°) unit cell parameters found to coexist with the first (with c = 30.21, $\beta =$ 90.28°, see Table 2). This included the structure solution, insertion of O and H atoms and of the SDA molecules, DFT optimization, and calculation of NMR chemical shifts. Identical results were obtained (within 0.3 eV for the energies, 0.2 ppm for ²⁹Si and ¹H RMSD, 0.5 ppm for ¹³C), leading also in this case to a unique best candidate model extremely similar to structure V. These two models of the molecular structure of CLS-1 are overlapped for comparison in Supporting Information, Figure S8. There appears to be vacant space available between the SDA molecules in both models for the water molecules (nearly two per SDA molecule) detected by ¹H NMR and TGA.

The strong advantage offered by the simple intralayer point of view of solid-state NMR is further illustrated when the situation at longer length scales is re-examined in light of the models derived from local structural information. In particular, the CLS-1 material appears to present considerably stronger extents of medium- to long-range stacking disorder than the numerous sharp reflections present on the diffraction data suggest. Strong indications of this stacking disorder is revealed by back-calculations of the diffraction data from our best structural models (superposition of two phases with SDA



Figure 7. Correlation plots between experimental and calculated (a) 29 Si, (b) 1 H, and (c) 13 C chemical shifts for DFT-optimized candidate model CLS-1 structures I to VI. DFT calculations are conducted with periodic boundary conditions using the GIPAW approach. Assignments of experimental 13 C NMR signals in part c were obtained by comparisons with empirical simulations of liquid-state NMR data and confirmed by 2D 13 C{ 1 H} solid-state correlation NMR spectra (data not shown).

molecules arranged as in model structure V), which fail to satisfactorily reproduce the intensities of the experimental XRD data (see Supporting Information, Figure S9), including with water O sites incorporated in the models (data not shown). This is in marked contrast with the excellent agreement of our best models with all other experimental data, with the exception of the omission of water molecules, which certainly account in part for the discrepancies between calculated and experimental diffraction patterns. Another reason is that the structural changes and obvious disordering that occur with increasing temperatures (see variable-temperature XRD data in Figure 3) may in fact be an amplification of a situation that already exists at room temperature. Specifically, the splitting and then collapse of (11l) reflections as well as shifts and broadening of (00l) reflections take place precisely in the temperature range (between 70 °C and 110 °C) where dehydration of the sample occurs. This suggests that leaving water positions vacant tends to cause a disordering of SDA positions and orientations (e.g., by quenching reorientation dynamics processes that involve water molecules) that has strong repercussions on the stacking order. Similarly, it is possible that heterogeneities in local water content (and/or positions of H₂O molecules) at room temperature may also be associated with some degree of stacking disorder that already affects the intensities of all but (*hk*0) reflections.

Furthermore, it seems clear that such variability (through disorder or polymorphism) in the sheet assemblies, whether in the form of disorder or superposition of slightly distinct phases, will necessarily be accompanied, at the local level, by variability in the relative positions and orientations of the SDA (and water) molecules with respect to the adjacent layers. This local disorder (whether static or dynamic) may very well be accounted for by some of the higher-energy SDA configurations discussed above, plus a number of others that were not allowed in our geometry optimizations because of the symmetry operations and periodic boundary conditions imposed by the space group. This space group indeed corresponds to symmetries of the average long-range structure, which might in fact involve multiple sites with partial occupancies for the SDA and water molecules. But these symmetry constraints do not necessarily have to be fulfilled at the local level. For example, these restrictions make it particularly difficult, if not impossible, to construct models in which the pyridine rings of two (or more) adjacent SDA molecules align (along the a direction) to form a $\pi - \pi$ interaction, which intuitively seems favorable.

It is clear that extensive further work would be needed to fully account for the stacking and local disorder, multiple phases, and water molecules present in this material. Dedicated programs exist (see for example ref 93) to model the effects of stacking disorder in layered materials, and the models established here based on the local structural constraints derived from DFT, NMR, and calculation data will provide an excellent starting point for future work in this direction.

3.d. Comparisons with Other Layered Silicate Materi**als.** From the point of view of the layered framework structure, a remarkable feature of the CLS-1 material studied here is its complete analogy in terms of topology (number of inequivalent Q³ and Q⁴ sites and Si–O–Si connectivities) to several other silicate materials with radically distinct morphologies. For example, surfactant-directed layered silicates (SDLS) prepared in basic hydrothermal conditions using $C_{16}H_{33}Me_2EtN^+$, $C_{16}H_{33}Et_2MeN^+$, or $C_{16}H_{33}Et_3N^+$ surfactants as SDAs exhibited short-range molecular order in their frameworks.^{1,53} One of these materials is represented schematically in Figure 8a, using the framework structure established in ref 56. As for CLS-1, ²⁹Si NMR analyses revealed that the silicate frameworks of these SDLS, shown in red in Figure 8d, consist of five equally populated inequivalent ²⁹Si sites, including two Q³ and three Q⁴ moieties, with the exact same set of Si–O–Si interconnectiv-ities^{43,53,56} as in CLS-1. Yet the SDLS and CLS-1 materials are profoundly different in several respects. First, the SDLS materials completely lack the long-range molecular order that was found for the CLS-1 material. In the former, the layers are separated by long and flexible surfactant chains that result in complete turbostratic disorder (i.e., complete translational and rotational disorder between two subsequent layers), accompanied at room temperature by fast (at the NMR time-scale)



Figure 8. (a, b, e, f) Schematic representations (a, f), model structures (b) or crystal structures (e) of different materials having layered silicate frameworks similar to that of the CLS-1 material studied here (in b). The resemblance between the silicate frameworks of the surfactant-directed layered silicate mesophases (SDLS, in red), CLS-1 materials (in green), and crystalline HUS-2 (ref 14, in blue) is illustrated in part c by the superimposition of their structures viewed from above the layers. All materials yield as a result similar ²⁹Si NMR signatures (c), each with five distinct crystallographic sites, albeit with different ²⁹Si chemical shifts due to distinct interactions between their respective organic structure directing agents and the silicate frame-

Figure 8. continued

work. The framework structure and simulated ²⁹Si spectrum shown in parts c and d were obtained after DFT optimization of the powder-XRD structure reported in ref 14 with water molecules omitted. (f) A similar framework has been detected at intermediate stages of the formation of MFI-zeolite nanosheets (see ref 94), as illustrated in the corresponding ²⁹Si NMR spectrum shown in yellow in part d (courtesy: Robert J. Messinger).

surfactant dynamics.⁸⁶ In the CLS-1 material, in contrast, small and comparatively rigid SDA molecules lead to high degrees of long-range molecular order, although some variability in the stacking and interlayer arrangement remains.

However, despite such radical differences, these two types of materials have very similar ²⁹Si NMR signatures (Figure 8d, spectra in red and green), which reflect identical framework topology. The first reason for such a paradox is that, as discussed above, solid-state NMR provides a local and essentially intralayer point of view. The second reason is that, at the molecular level, the framework molecular structures of CLS-1 and the surfactant-templated material are in fact extremely similar, if not identical. This is illustrated in Figure 8c, which shows a superposition of the framework structure of CLS-1 (in green) and one of the framework structures established for the C16H33Me2EtN+-silicate (in red) using a similar approach as described here for CLS-1.56 Because of limitations in the modeling of the surfactants in particular, it was not possible in the case of the SDLS to ultimately distinguish between the final three structures, all topologically identically and structurally close. One of them, referred to as structure ${\bf 2}$ in the corresponding paper^{56} and shown in red in Figure 8d, overlays particularly well with the CLS-1 framework.

The strong propensity of what appears to be a common framework to crystallize under various conditions (acid and basic pH, very distinct SDA morphologies, etc.) is further illustrated by two other examples. The crystalline HO-CH₂- $CH_2 - N(CH_3)_3^+$ -directed HUS-2 material,¹⁴ whose structure (shown in Figure 8e) was determined from powder X-ray diffraction data, also yields a ²⁹Si NMR spectrum (²⁹Si peak positions shown in pale blue in Figure 8d) remarkably similar to that of the CLS-1 and SDLS materials. While the stacking of the layers in our CLS-1 models (Figure 8b) and in the crystal structure of HUS-2 (Figure 8e) are clearly different, with the central layer shifted by half a unit cell in HUS-2, their framework structures again superimpose remarkably well. In fact, they superimpose even more closely if, instead of considering the reported HUS-2 structure, refined against powder XRD data, we use a structure that is first relaxed with DFT (leaving the partially water positions unoccupied for simplicity), as shown in blue in Figure 8c. This DFT-optimized structure of HUS-2 yields calculated ²⁹Si parameters (blue simulated spectrum in Figure 8d) in considerably better agreement with experimental data¹⁴ than the original powder-XRD structure, as illustrated in Supporting Information, Figure S10. (Such inaccuracies in the atomic positions of the reported HUS-2 structure are attributed primarily to the low sensitivity of powder X-ray diffraction to oxygen atom positions.) Hence, completely different structure-determination protocols applied to very distinct materials all converge to a single layered framework type, which confirms the robustness of the approaches based on local structural constraints used here and in ref 56.

Maybe even more interesting is the discovery recently made by some of us⁹⁴ that a similar ²⁹Si NMR signature (shown in yellow in Figure 8d) appears in the intermediate stages of the formation of mesostructured zeolite silicalite-1, the siliceous analogue of aluminosilicate zeolite catalyst ZSM-5 (MFI-type structure).^{2,3,95} Under the action of the (CH_3) - $(CH_2)_5 N^+ (CH_3)_2 (CH_2)_6 N^+ (CH_3)_2 (CH_2)_{21} (CH_3)$ diquaternary ammonium surfactants, several interesting atomic- and mesoscale structural transformations occur within the same particle domains, as summarized in Figure 8f. The hexagonal mesophase formed in the first days of the synthesis then crystallizes into a lamellar phase with thin layers identical to those of the SDLS materials. Groups of layers within this structure then progressively transform into 2.7 nm thick MFI zeolite sheets via a nontopotactic process (although both frameworks are shown to coexist in nanometer-scale domains).⁹⁴ Only now could the molecular structures of the new CLS-1 and the long-existing surfactant-directed materials be solved with the introduction of a novel protocol, taking full advantage of the long-range information provided by diffraction techniques and the full set of short-range structural constraints provided by solid-state NMR, in combination with DFT calculations.

4. CONCLUSIONS

The framework structure of a new layered silicate material, CLS-1, of composition $[Si_5O_{11}H][C_9N_2H_{15}]\cdot 1.9(H_2O)$, was determined despite complicated extents of disorder in its sheet assemblies. This was made possible by the combination of two crystallographic approaches. The classical approach, based on diffraction techniques (electron and synchrotron X-ray) probing long-range atomic order, led to the identification of a set of possible space groups but failed to provide a sufficient basis for solving the structure, due to incomplete stacking order of the silicate sheets. Solid-state NMR, in contrast, is largely insensitive to the long-range interlayer order and provides local information on the framework structure, from which structural models can be established. These models are generated through a comprehensive search for possible framework structures that are consistent with local structural constraints provided by ²⁹Si NMR data: the number, nature $(Q^3 \text{ or } Q^4)$, and multiplicities of tetrahedral SiO₄ sites, their Si-O-Si connectivities, and multiple Si-Si distance information. Among the different space groups identified, only one $(C_{2/C}$, no. 15) was proved compatible with both the long- and short-range information obtained at room and variable temperatures, leading to three distinct but structurally close framework structure solutions. The organic structure-directing agent was then inserted at different orientations and positions in the interlayer space, after which the structures were relaxed by DFT. Comparisons of calculated and experimental ¹H, ¹³C, and ²⁹Si chemical shifts led to the identification of a single structural model that best accounts for the otherwise complicated molecular structure of CLS-1. While there is clear evidence that the relative organization of the layers and orientations of the SDA molecules in the interlayer spaces are intrinsically far richer than in our simplified model, our approach nevertheless led to the unique determination of the silicate framework. This framework structure turns out to be essentially similar to that of several other layered silicates with very diverse morphologies and extents of stacking order, underlying a strong propensity of this new framework structure to form under a broad range of synthesis conditions and structure-directing agents. In particular, the recent discovery that this exact silicate framework forms in intermediate stages of the formation of technologically important nanostructured MFI zeolite⁹⁴ suggests that the CLS-1 material, like other materials sharing the same silicate framework^{1,14,53,56} is potentially capable of undergoing a solidstate transformation, which opens the way to new zeolite synthesis routes.

ASSOCIATED CONTENT

Supporting Information

Details of the pseudopotentials used for DFT calculations (Table S1). List of model crystal systems used for the referencing of calculated chemical shifts (Table S2). Correlation plots between experimental chemical shifts and calculated shielding on model crystal systems (Figure S1). Powder synchrotron XRD patterns of CLS-1 samples B and C. TGA analyses conducted on CLS-1, sample B (Figure S4). NMR ¹⁹F MAS spectrum of CLS-1, sample B (Figure S5). Superposition of framework structures generated from ²⁹Si NMR data with O and H atoms added and refined (Figure S6). Superposition of the six DFT-optimized candidate model structures of CLS-1 with C2/c space group and $\beta = 90.279^{\circ}$ (Figure S7). Table of γ^2 values giving the agreement between experimental and calculated NMR chemical shifts (Table S3). Superposition of the best model structures established with the two distinct sets of unit cell parameters (Figure S8). Rietveld refinement vs XRD data based on the best model structures of CLS-1 (Figure S9). Comparisons of the silicate frameworks and calculated ²⁹Si NMR spectra of reported and DFT-optimized HUS-2 structures (Figure S10). Atomic coordinates of best model structures in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: sylvian.cadars@cnrs-orleans.fr.

Notes

The authors declare no competing financial interest.

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