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Hydrothermal synthesis and crystal structure of a new three-dimensional aluminum-organic framework MIL-69 with 2,6-naphthalenedicarboxylate (ndc), Al(OH)(ndc)·H₂O

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Abstract

A new three-dimensional aluminum-organic framework, MIL-69 or Al(OH)(O$_2$C–C$_{10}$H$_6$–CO$_2$)·H$_2$O, has been hydrothermally synthesized at 210 °C for 16 h, by using 2,6-naphthalenedicarboxylic acid as a rigid ligand. The model for the crystal structure of MIL-69 was determined by means of lattice energy minimizations and further refined against the powder XRD data using the Rietveld refinement method. The crystal structure consists of infinite chains of AlO$_4$(OH)$_2$ octahedra corner-linked through the μ$_2$-hydroxyl groups and connected by the 2,6-naphthalenedicarboxylate moieties. It results in the formation of flat channels parallel to the chains of aluminum octahedra, running along the c axis. A water molecule is trapped nearby the center of the tunnels and mainly interacts via hydrogen bonds with the hydroxyl groups and the oxygen atoms of the carboxylates. Although the three-dimensional aluminum-organic framework is stable up to 450 °C, the tunnels still remain shrunk upon removal of water molecule, because of the occurrence π–π interactions between the naphthalene groups. The MIL-69 phase was characterized by solid state NMR MAS ^{27}Al, ^{1}H and ^{13}C{^{1}H-decoupled}, which is consistent with the crystal structure description. **Crystal data. –** MIL-69, Al(OH)(O$_2$C–C$_{10}$H$_6$–CO$_2$)·H$_2$O: Mr = 267.11 g mol^{-1}, monoclinic, space group $C2/c$ (no. 15), a = 24.598(2) Å, b = 7.5305(6) Å, c = 6.5472(5) Å, $β$ = 106.863(8)°, V = 1160.6(2) Å^3, Z = 4. ***To cite this article: T. Loiseau et al., C. R. Chimie 8 (2005).***

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Résumé

Synthèse hydrothermale et caractérisation structurale d'un solide tridimensionnel à base d'aluminium et d'acide 2,6-naphthalènedicarboxylique, Al(OH)(ndc)·H₂O (MIL-69). Un nouveau composé tridimensionnel mixte aluminium-organique, MIL-69 ou Al(OH)(O$_2$C–C$_{10}$H$_6$–CO$_2$)·H$_2$O, a été synthétisé par voie hydrothermale à 210 °C pendant 16 heures, en utilisant l'acide 2,6-naphthalènedicarboxylique comme ligand rigide. Le modèle utilisé pour la détermination structurale est obtenu à l'aide de calculs de minimisation d'énergie et ensuite affiné avec les données de diffraction de rayons X du diagramme

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de poudre (méthode Rietveld). La structure est construite à partir de chaînes infinies d'octaèdres $AlO_4(OH)_2$ liés entre eux par sommets via les groupements μ_2-hydroxyles, et connectées par les ligands 2,6-naphthalènedicarboxylates. Cet arrangement atomique génère la formation d'un réseau comportant des tunnels aplatis se propageant suivant la direction parallèle aux chaînes d'octaèdre d'aluminium, suivant l'axe c. Une molécule d'eau est piégée au centre des tunnels et interagit principalement avec les groupements hydroxyles et les atomes d'oxygène des carboxylates par l'intermédiaire de liaison hydrogène. Bien que la charpente tridimensionnelle mixte aluminium-organique soit stable jusqu'à 450 °C, les tunnels restent contractés lors du retrait de la molécule d'eau, en raison de l'existence d'interactions π–π entre les groupements naphtalène. La phase MIL-69 a été caractérisée par RMN MAS du solide (^{27}Al, ^{1}H et ^{13}C{^{1}H-découplé}) et est en accord avec la description structurale proposée.

1. Introduction

The synthesis of hybrid inorganic–organic porous solids or metal-organic frameworks (MOF-*n*) has recently grown exponentially, giving rise to the formation of new nanoporous materials with very high surface area [1–3]. The combination of the huge variety of possible organic linkers and the multiple physical properties of inorganic cations, allow a wide modulation of both the dimensions of the pores and the properties of the final porous compounds. In such structures, organic species (amines, carboxylates...) can act either as pillars, linkers and arrange, respectively, inorganic layers, chains or clusters of transition or rare-earth metals [4–9]. Usually rigid ligands containing aromatic ring are associated with mono or divalent metals, resulting in the construction of new architectures with different dimensionalities of pore system. Some of these materials exhibit significant properties in the field of gas adsorption [10,11]. For instance, the solid MOF-5 was recently found to be an excellent candidate for the methane [12] or hydrogen [13] adsorption.

We recently initiated a global study of the reactivity of trivalent metals (V^{3+} [14–18], Cr^{3+} [19], Fe^{3+} [20,21]) with aromatic dicarboxylic acids in water under mild hydrothermal conditions. We then extended this work to the *p* metal elements such as aluminum, gallium or indium. Up to now, the utilization of such cations was rarely reported in the literature since only the indium terephthalate $In_2(OH)_3(bdc)_{1.5}$ [22] and the alu-minum terephthalate MIL-53 [23] ($Al(OH)(bdc)\cdot xH_2O$, isostructural to the vanadium [14] and chromium [19]-based phases) were isolated (bdc = 1,4-benzenedicarboxylic acid). The latter was also tested for its hydrogen adsorption capacity and it can adsorb up to 3.8 wt.% of H_2 under 16 MPa at 77 K [24]. This promising feature of MIL-53 incited us to continue our systematic study with other carboxylic acids and we report here the hydrothermal reaction of the another connector, 2,6-naphthalenedicarboxylic acid, with aluminum. This aromatic carboxylic acid was previously used with divalent metals such as Zn [25–27], Mn [26], Cd [26] and rare-earth metals such as Ce [28], Eu [28], Tb [28], Er [29], Yb [30]. The synthesis and the structural characterization of a new aluminum 2,6-naphthalenedicarboxylate called MIL-69 ($Al(OH)(O_2C–C_{10}H_6–CO_2)\cdot H_2O$ are presented.

Indeed, simulations methods are particularly useful for predicting possible crystal structures of inorganic [31,32] and hybrid structures [33,34] and help the difficult process of structure determination. Here, an original simulation method is used in order to anticipate a possible crystal structure for MIL-69, starting with the knowledge of the existing MIL-53 structure and considering that very similar synthetic conditions than in MIL-53 were used. A structural model was proposed and further refined from the powder X-ray diffraction technique. The compound was further characterized by solid state NMR (^{27}Al, ^{1}H, ^{13}C). MIL-69 exhibits a three-dimensional framework consisting of channels

bound by infinite aluminum octahedra chains and 2,6-naphthalenedicarboxylate groups, encapsulating a water molecule.

2. Experimental procedure

2.1. Synthesis

Al(OH)(O$_2$C–C$_{10}$H$_6$–CO$_2$)·H$_2$O (MIL-69) was synthesized hydrothermally in a 23 ml Teflon-lined bomb Parr under autogeneous pressure. The starting reactants were aluminum nitrate (Al(NO$_3$)$_3$·9 H$_2$O, Carlo Erba Regenti, 98%), 2,6-naphthalenedicarboxylic acid (HO$_2$C–C$_{10}$H$_6$–CO$_2$H, Avocado, 98%, hereafter noted *ndc*), potassium hydroxide (KOH, Aldrich, 90%) and distilled water. The molar ratio was 1 Al (3.5 mmol, 1.314 g); 0.5 *ndc* (1.75 mmol, 0.3783 g); 1.2 KOH (4.35 mmol, 0.2440 g); 80 H$_2$O (277.8 mmol, 5 ml). The reaction pH was 1–2. The mixture was placed in the autoclave at 210 °C for 16 h, which are the optimized conditions for the synthesis of the titled compound. For longer reaction times (24, 36 or 48 h), the formation of the aluminum oxyhydroxide AlO(OH) (boehmite form) was observed together with MIL-69. When the reaction time increases, the MIL-69 phase progressively disappears indicating its dissolution during the hydrothermal treatment and the aluminum re-crystallizes under the AlO(OH) form. A kinetic study of the hydrothermal reaction showed that maximal yield of formation of MIL-69 is observed for 16 h. It was 75% based on aluminum. For shorter reaction times, an additional unknown minor phase with Bragg peaks at 5.78 and 3.31 Å appears with MIL-69. The presence of KOH is required for setting the pH value around 1–2 otherwise a mixture of the phases MIL-69 and AlO(OH) is systematically observed. The obtained crystalline product was filtered off, washed with distilled water and dried at room temperature. Scanning electronic microscope examination showed that samples of MIL-69 consist of a very fine powder with grain sizes lower than 1 μm.

2.2. Simulations and structure solution

The structure of Al(OH)(O$_2$C–C$_{10}$H$_6$–CO$_2$)·H$_2$O (MIL-69) was determined from structural computer simulation and laboratory powder X-ray diffraction data. The diffraction intensities were collected on a Siemens D5000 diffractometer (θ–2θ mode, step size: 0.02°(2θ), time acquisition/step: 65 s) using the Cu Kα radiation (λ = 1.5418 Å) at room temperature, between 6 and 76°(2θ). By using the DICVOL91 [35] software, a monoclinic cell with satisfactory figures of merit was found for MIL-69, with cell parameters of a = 24.6254 Å, b = 7.5285 Å, c = 6.5597 Å, β = 106.791°, V = 1164.27 Å^3 (obtained with the figures of merit M_{11} = 56.9 and F_{11} = 57.6 (0.0035, 54)). The examination of the systematic extinctions led to the space group C2/c or Cc.

Then, lattice energy minimizations were used with the aim of anticipating the crystal structure of the MIL-69 compound. Considering that similar synthetic conditions were used than in for the synthesis of MIL-53, particularly regarding the organic: metal ratios, and also the similarity of cell parameters between MIL-53 and MIL-69, we assumed that a similar framework topology to that of aluminum terephthalate MIL-53 might occur in the aluminum naphthalate, MIL-69, with the aim of simply replacing the 1,4-bdc acid by the 2,6-ndc acid. Starting from the crystal structure of the as-synthesized aluminum terephthalate MIL-53 [23] in the *C*2/*c* space group, a model for the MIL-69 was derived as follows in the *C*2/*c* space group: the aromatic rings of the terephthalate molecules were removed from the MIL-53 structure file, while keeping the carboxylate functions. Such a modification left us with the infinite aluminum octahedra chains typical of the MIL-53 topology, where each aluminum atom is still fully coordinated with terminal water molecules and oxygen atoms of the carboxylic functions. The intermediate model was then submitted to a cell extension along the *a* axis (from 19.5 Å in MIL-53 [23], to 24.6 Å in MIL-69) which corresponds to the move of the chains away from each other, leaving the required space for the insertion of 2,6-naphthalenedicarboxylic acid. The naphthalene aromatic rings were inserted between the chains, while using the carboxylic functions as anchorage points so that the naphthalene molecule are placed in a similar way than in the MIL-53 topology. Finally, the constructed model was submitted to a full lattice energy minimization, allowing all atoms to relax while keeping the cell parameters fixed at the experimental values, using the universal forcefield [36] and *Cerius2* software suite [37]. The minimizations rapidly converged towards a plausible crystal structure.

The atomic coordinates predicted by the simulations were then directly used as a starting model in our Rietveld refinement. The pattern matching procedures were performed with Fullprof2k using the WinPLOTR software package [38]. The final reliability factors including 47 refined parameters and 386 independent reflections are $R_P = 0.122$, $R_{WP} = 0.140$, $R_B = 0.0622$ and $R_F = 0.0566$ with the following cell parameters: $a = 24.598(2)$ Å, $b = 7.5305(6)$ Å, $c = 6.5472(5)$ Å, $\beta = 106.863(8)°$ and $V = 1160.6(2)$ Å^3. The corresponding Rietveld plot is reported in Fig. 1. Atomic coordinates and selected interatomic distances of MIL-69 (Al) are given in Tables 1 and 2, respectively. The chemical formula deduced from the structure determination is $Al(OH)(O_2C–C_{10}H_6–CO_2)\cdot H_2O$
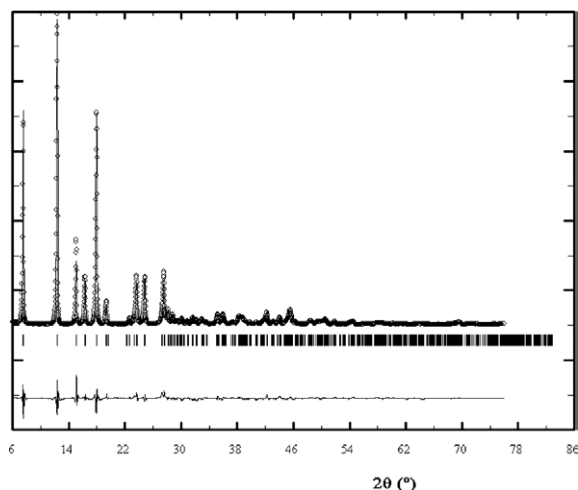
Fig. 1. Final Rietveld plot of $Al(OH)(O_2C–C_{10}H_6–CO_2)\cdot H_2O$ (MIL-69). The observed data are shown by the open circles and the calculated data by the solid line.

Table 1
Atomic coordinates of $Al(OH)(O_2C–C_{10}H_6–CO_2)\cdot H_2O$ (MIL-69)

Atom	Wyckoff position	x	y	z
Al	4a	0	0	0
O1	4e	0	–0.099(1)	3/4
O2	8f	0.0465(3)	–0.825(1)	0.654(1)
O3	8f	0.0678(4)	–0.8618(9)	0.984(1)
Ow	4e	0	–0.458(1)	3/4
C1	8f	0.1442(3)	–0.769(2)	0.857(2)
C2	8f	0.1835(3)	–0.812(2)	0.068(1)
C3	8f	0.2803(4)	–0.818(2)	0.290(2)
C4	8f	0.0870(4)	–0.824(2)	0.828(2)
C5	8f	0.242(4)	–0.797(2)	0.080(2)
C6	8f	0.3390(3)	–0.794(2)	0.307(2)

Table 2
Selected interatomic distances (Å) in $Al(OH)(O_2C–C_{10}H_6–CO_2)\cdot H_2O$ (MIL–69)

Al–O1 = 1.780(4)	C1–C2 = 1.48(1)
Al–O2 = 1.845(8)	C1–C6 = 1.34(1)
Al–O3 = 1.994(9)	C2–C5 = 1.44(1)
O2–C4 = 1.28(1)	C5–C3 = 1.43(1)
O3–C4 = 1.28(1)	C5–C5 = 1.40(2)
C4–C1 = 1.43(1)	C3–C6 = 1.43(1)
Ow···O1 = 2.70(1)	

and is in agreement with the elemental analysis (CNRS Analysis Center, Vernaison, France): Al: obs.: 9.7% (calc.: 9.8%); C: obs.: 3.4% (calc.: 3.3%); H: obs.: 3.4% (calc.: 3.3%). Density measurement gave 1.606(5) g cm^{-3} (calc.: 1.529 g cm^3).

2.3. Solid-state NMR

NMR spectra were acquired on a Bruker Avance 500 spectrometer with a 11.7 T field, equipped with a Bruker 4 and 2.5 mm probes, with resonance frequencies for ^1H, ^{13}C and ^{27}Al of 500.13, 125.77, and 130.32 MHz, respectively. Typically, $\pi/4$ pulse widths of 2.1 μs, repetition times of 2 s, and spectral widths of 100 kHz were used for single pulse ^1H MAS experiments. The MAS speed employed was 30 kHz. The Hahn echo pulse sequence was performed for ^{27}Al MAS experiment using selective pulses with a $\pi/2$ pulse length of 1 μs corresponding to a radiofrequency strength of 83 kHz, and a relaxation delay of 1 s. The experiment was synchronized with rotation speed (30 kHz), for which an echo delay of 2.33 ms corresponding to the fid length was set. ^{13}C MAS spectra were acquired using a 4-mm ZrO_2 rotor under conditions of high-power proton decoupling using a pulse length of 5.9 μs ($\pi/2$), a repetition delay of 20 s, a rotation rate of 12.5 kHz, and decoupling power of 9 kHz. All spectra were referenced relative to standards tetramethylsilane for ^1H and ^{13}C NMR and $Al(NO_3)_3$ aqueous solution for ^{27}Al using adamantane (1.74 ppm for ^1H and 38.3 ppm for ^{13}C) and $NH_4Al(SO_4)_2\cdot12\,H_2O$ (–0.6 ppm for ^{27}Al) as secondary references. Decomposition of spectra was achieved using the dmfit2004 NMR simulation software [39].

3. Description of the structure

The structure of $Al(OH)(O_2C–C_{10}H_6–CO_2)\cdot H_2O$ (MIL-69) consists of a three-dimensional framework
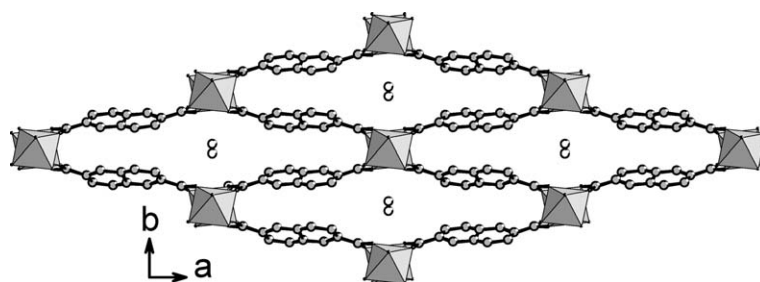
Fig. 2. Representation of the structure of $Al(OH)(O_2C-C_{10}H_6-CO_2)\cdot H_2O\cdot(MIL-69)$ showing the channels running along *c* and encapsulating water molecules (open circles). Grey octahedra: $AlO_4(OH)_2$.

built up from the connection of infinite chains of corner-sharing octahedral $AlO_4(OH)_2$ units with naphthalate ligand *ndc* (Fig. 2). The aluminum cation (on special position 4*a*) is octahedrally coordinated to four oxygen atoms from the carboxylic function and two hydroxyl groups located in *trans* position. The Al–O distances are 1.845(8) and 1.994(9) Å, and Al–OH one is 1.780(4) Å (Fig. 3). Bond valence calculations [40] give values of 1.41 and confirm the occurrence of a μ_2-hydroxide anion for the bridging oxygen O1. The result-
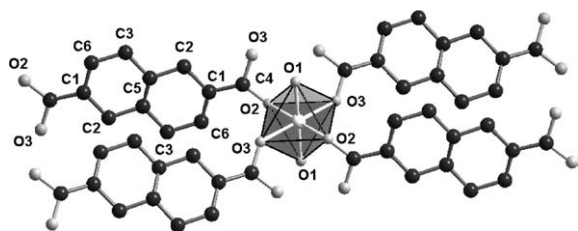

Fig. 3. Coordination surrounding with atoms labels for the unique crystallographically aluminum cation.

ing $AlO_4(OH)_2$ units are linked to each other through the two opposite hydroxyl groups and this generates an infinite chain of corner-sharing octahedra running along the *c* axis. The files of octahedra are connected to each other through the naphthalenedicarboxylate molecules. The carboxylate ion, $R\text{-}CO_2^-$, acts as a bridging bidentate ligand adopting an usual *syn–syn* configuration [41,42]; the oxygen atoms of each carboxylic acid function are linked to two consecutive aluminum atoms (Fig. 4). This particular connection mode gives rise to the formation of a three-dimensional organic-inorganic network with flat channels running along the *c* axis, parallel to the $AlO_4(OH)_2$ chains. The accessible pore size of this one-dimensional tunnel is approximately 2.7 × 19.4 Å (it was taken into account the oxygen radius of 1.35 Å) and does not include significant void. However, a water molecule is trapped nearby the center of the tunnels (at the special position 4*e*, 0 0.458(1) 3/4). It mainly interacts with the bridging hydroxyl groups ($d_{Ow\cdots O1}$ = 2.70(1) Å) and the oxygen atoms of

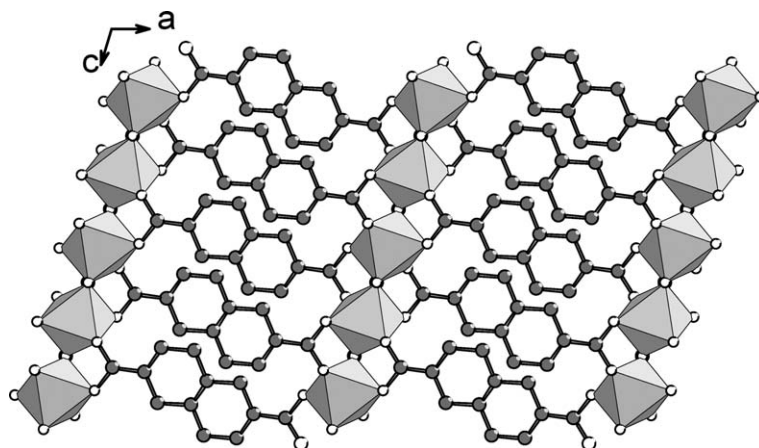Fig. 4. Representation of the structure of $Al(OH)(O_2C-C_{10}H_6-CO_2)\cdot H_2O$ (MIL-69) showing the infinite chains of $AlO_4(OH)_2$ units (gray octahedra) connected via the 2,6-naphtalenedicarboxylate ligand along *c*.

carboxylic acids $d_{Ow...O2} = 3.12(1)$ Å). Weak π–π interactions ($d_{C...C} \approx 3.9$ Å) are also observed between the aromatic rings of two adjacent naphthalate species along the b axis. The occurrence of the hydrogen bond interactions together with the π–π ones contributes to the shrinkage of the channels along the b axis. A similar flat tunnel shape is also observed in the ytterbium-*ndc* framework CUmof-9 [30].

Such an atomic arrangement of octahedra-based chains is obviously reminiscent to that encountered in the compound series synthesized in the presence of 1,4-benzenedicarboxylic acid with aluminum [23] (MIL-53), chromium [19] (MIL-53) or vanadium (MIL-47 [14] and MIL-68 [17]). In these compounds, identical infinite $MO_4(OH)_2$ files are observed and are connected to each other via the terephthalate ligand instead of 2,6-naphthalenedicarboxylate one. The same structure of MIL-69 was also obtained with vanadium replacing aluminum [43].

TG experiments were performed under nitrogen with heating rate of 3 °C min^{-1} between room temperature and 800 °C using a TA Instrument TG2050 apparatus. The thermogravimetric analysis (Fig. 5) indicates that water can be removed upon heating below 100 °C (obs.: 6.1%; calc.: 6.9%). The water weight loss is reversible and the product rapidly re-adsorbs water in air atmosphere. The solid is thermally stable up 450 °C and then a second weight loss is observed. It is assigned to the departure of the 2,6-naphthalenedicarboxylate ligand together with the collapse of the structure (obs.: 67.2%; calc.: 74.0%). At 800 °C, the XRD pattern shows that the product is amorphous. The vanadium [43] analog of MIL-69 showed no cell parameter modification on water removal. This is in contrast with the breathing phenomenon encountered in the parent series of MIL-53
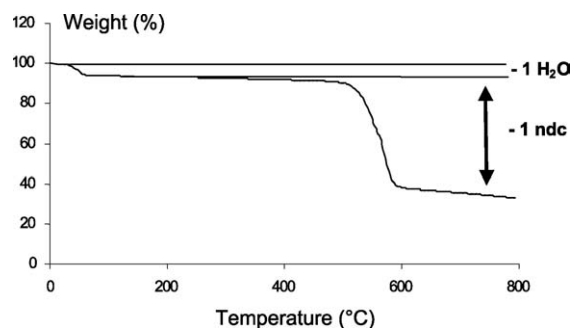

Fig. 5. TG curve of Al(OH)(O$_2$C–C$_{10}$H$_6$–CO$_2$)·H$_2$O or MIL-69 under N$_2$ (heating rate 3 °C min^{-1}).

(Cr [19], Al [23]). Flat lozenge-shape tunnels (2.6 × 13.6 Å^2) were observed in the hydrated form, in which a water molecule is engaged in the hydrogen bond interactions with anions of the hybrid network. In the anhydrous form, the tunnels become larger (8.5 × 8.5 Å^2) and exhibit a square-like shape. The origin of these two different structural behaviors might come from the existence of π–π interactions between the aromatic ligands, which are stronger for the naphthalene-based molecule than those of the single aromatic ring of the terephthalate ligand. Concerning the MIL-69 (Al) phase, a study of its thermal behavior is currently in progress in order to characterize the cell expansion when water molecules are removed from the structure pores.

4. Solid-state NMR of MIL-69

The ^{27}Al 30 kHz-MAS NMR spectrum indicates a unique resonating signal with a powder pattern indicative of second-order quadrupolar interaction (Fig. 6). Simulation of the line shape (bottom pattern in Fig. 6) results in a quadrupolar coupling constant of 11.1 MHz, an asymmetry parameter of 0.17 and an isotropic chemical shift value of 3.1 ppm, confirming aluminum is octahedrally coordinated. These findings strictly agree with structure analysis for which, only one crystallographic site is found for aluminum with an octahedral coordination.

The ^{1}H 30-kHz MAS NMR spectrum exhibits a broad signal, which can be decomposed into four components (Fig. 7). The most intense signal at 7.0 ppm is
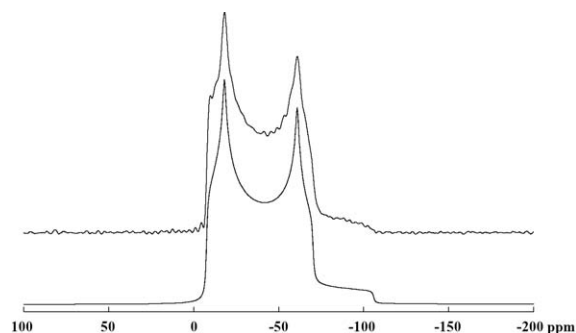

Fig. 6. Experimental Hahn echo ^{27}Al MAS NMR spectrum (top) of MIL-69 acquired at a spinning speed of 30 kHz. The simulated spectrum (bottom) using a powder model with an isotropic chemical shift δ_{iso} of 3.1 ppm, a quadrupolar coupling constant C_Q of 11.1 MHz, and an asymmetry parameter η of 0.17.
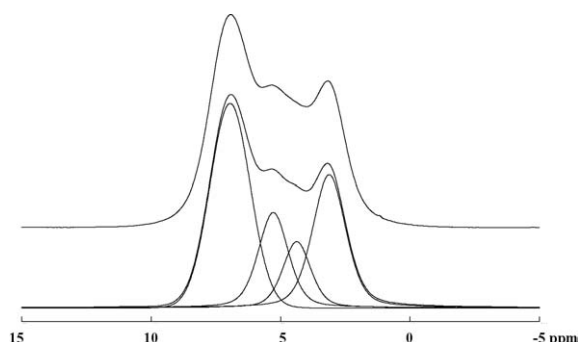
Fig. 7. Experimental ^{1}H MAS NMR spectrum (top) of MIL-69 collected at a spinning speed of 30 kHz. The simulated spectrum and its decomposition are included (bottom) showing four components at 7.0 ppm (46%), 5.3 ppm (18%), 4.4 ppm (11%) and 3.1 ppm (27%).

assigned to hydrogen belonging to the benzene rings of the 2,6-naphthalenediacarboxylate, as expected for this chemical shift value. The peaks at 5.3 and 4.4 ppm could correspond to the hydrogen of the water molecules. Only one water species is observed in the structure and the occurrence of the two contributions for water may result from two locally inequivalent environments for the encapsulated molecule. The fourth signal is assigned to the μ_2-hydroxyl group, bridging the aluminum cations to each other. It is noted that no resonating line is observed in the range 10–15 ppm relating to the protonated carboxylic acid R-CO$_2$H, as expected from the structure analysis.

The ^{13}C{^{1}H-decoupled} MAS NMR spectrum shows two groups of signal at 176 and 134 ppm (Fig. 8). The peak resonating at 176 ppm corresponds to the carbon of the carboxylate R-CO$_2^-$ and the broader line at 134 ppm is assigned to the different carbon atoms of the two aromatic rings of the naphthalene species.
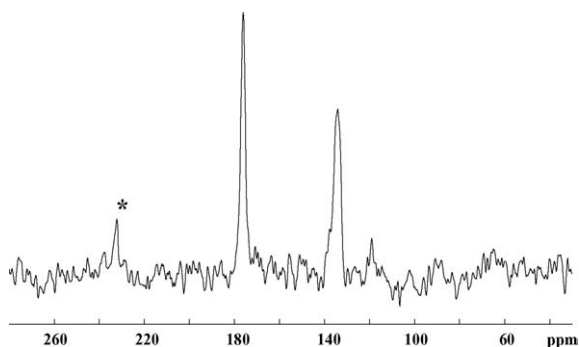

Fig. 8. ^{13}C{^{1}H} high-power decoupling MAS spectrum of MIL-69 acquired at a spinning speed of 12.5 kHz. The star denotes satellite side band.

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