Hydrothermal synthesis and structural characterization
of a gallium pyromellitate Ga(OH)(btec)-0.5H₂O,
with infinite Ga-(µ₂-OH)-Ga chains (MIL-61)

Thierry Loiseau a,*, Hervé Muguerra a, Mohamed Haouas a, Francis Taulelle a, Gérard Férey a, b

a Institut Lavoisier (UMR CNRS 8637) Université de Versailles St Quentin en Yvelines, 45, Avenue des Etats Unis, 78035 Versailles, France
b Institut Universitaire de France, France

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Abstract

A new gallium carboxylate Ga(OH)(btec)-0.5H₂O (MIL-61) was synthesized under mild hydrothermal conditions (200 °C, 24 hours) in the presence of 1,2,4,5-benzenetetracarboxylic (btec) acid and water. The crystal structure, characterized by means of Rietveld refinement of powder XRD data, consists of trans chains of GaO₄(OH)₂ octahedra, connected to each other through a µ₂-OH group. The three-dimensional framework is built up from these chains linked together via the organic molecules so delimiting the cavities where the water molecules are encapsulated. Analysis by solid state NMR (¹H and ¹³C) has confirmed the presence within the structure of both water molecules and carboxylate moieties partially deprotonated. The structure of Ga(OH)(btec)-0.5H₂O corresponds to that of MIL-61 obtained with vanadium replacing gallium.

Crystal data for Ga₄(OH)₄((HO₂C)₂–C₆H₄–(CO₂)₂)₄·2H₂O: a = 14.8325(10) Å, b = 6.7792(10) Å, c = 10.6726(10) Å, V = 1073.2(2) Å³, Pnma (n° 62).

Keywords: Hydrothermal synthesis; Gallium; 1,2,4,5-benzenetetracarboxylic acid; Metal-organic frameworks; X-ray powder diffraction; Solid state NMR; ¹H, ¹³C

1. Introduction

The synthesis of hybrid organic-inorganic compounds based on the connection of aromatic carboxylate ligand with metallic centers gives rise to the production of a large variety of frameworks with porous properties [1–6]. The structures of these compounds may be divided into two series: some of them are built up from isolated metallic clusters composed of single metal-centered polyhedra (tetrahedron, square pyramid, octahedron, ...) or arrangement of several polyhedral unit, i.e., paddle-wheel unit consisting of two square pyramids MO₅ for copper [7–9] or four tetrahedra MO₄ connected via a µ₄-oxygen for zinc [10,11]. In other solids, infinite polymeric chains, usually composed of MO₅ octahedra occur and are linked to each other through the carboxylate ligands. This was especially observed in compounds incorporating trivalent metals (V, Cr, Al, ...) [12–15] and sometimes in zinc crystal chemistry [16,17].

During the investigation of the synthesis of new gallium carboxylate phases, we prepared in the presence of pyromellitic acid, a new solid whose structure is related to the known vanadium(III) carboxylate compound, labeled MIL-61 [18]. In the previous report, two phases V₃II₂(OH)₂(C₆H₄–(CO₂)ₓ)·4H₂O (MIL-60) and V₃III(OH)((HO₂C)₂–C₆H₄–(CO₂)ₓ)·H₂O (MIL-61) crystallize under similar experimental conditions but the later requires higher amount of pyromellitic acid in the reactant composition, about 5 times what needed for the former. With the described conditions, we were unable to obtain the gallium isotype MIL-60

* Corresponding author. Tel.: +33 1 39 254 373; Fax: +33 1 39 254 358.
E-mail address: loiseau@chimie.uvsq.fr (T. Loiseau).

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phase, while the gallium equivalent MIL-61 was successfully formed. The present work deals with the preparation and crystal structure characterization of the MIL-61 gallium analog: Ga(OH)(HO2C-C6H4-CO2)0.5H2O or Ga(OH)(btec)-0.5H2O with btec = 1,2,4,5-benzenetetracarboxylic acid. Its powder X-ray diffraction refinement, thermogravimetric analysis and 13C and 1H NMR are presented.

2. Experimental

2.1. Synthesis

The gallium pyromellitate Ga(OH)(btec)-0.5H2O (MIL-61) was hydrothermally synthesized under autogenous pressure in the presence of 1,2,4,5-benzenetetracarboxylic acid and water. The starting reactants were gallium nitrate (Ga(NO3)3·xH2O, Aldrich, 96%), 1,2,4,5-benzenetetracarboxylic acid (C6H4(CO2H)4, Fluka Chemika, 97%) and distilled water. Typically, the reaction mixture containing the molar ratio 1 Ga (3.5 mmol, 0.8951 g), 0.5 btec (1.75 mmol, 0.445 g), 80 H2O (277.8 mmol, 5 ml) was placed in a 23 ml Teflon-lined steel Parr autoclave at 200 °C for 24 hours. The synthesis pH at the end of the reaction was 1. A white powdered product (yield: 75 %) was filtered off, washed with deionized water and dried in air at room temperature. Scanning electron microscope (Fig. 1) examination indicated that the sample is composed of small pseudo-octahedral crystals of homogeneous size around 2–3 µm. Preliminary X-ray powder diffraction pattern showed it to be a novel phase.

Some tries were also carried out in an attempt to obtain identical phase replacing gallium by aluminum but were not successful.

2.2. Structure analysis

The structure of Ga(OH)(btec)-0.5H2O (MIL-61) was determined using Rietveld refinement method from powder X-ray diffraction data since no suitable large enough single-crystal was available. The diffraction intensities were collected on a Siemens D5000 diffractometer (θ–2θ mode, step size: 0.02°(2θ), time acquisition/step: 80 s) using CuKα radiation (λ = 1.5418 Å) at room temperature, between 8 and 80°(2θ). By using the DICVOL91 software [19], an orthorhombic system, with cell parameters of a = 14.8325(10) Å, b = 6.7792(10) Å, c = 10.6726(10) Å, V = 1073.2(2) Å3, was found with satisfactory figures of merit M15 = 30.5 and F15 = 40 (0.0088, 42). Theses parameters are very close to that of vanadium isotope MIL-61 prepared with the same aromatic ligand V(OH)((HO2C)2–C6H4–(CO2)2)·H2O [18], recently synthesized in the laboratory (a = 14.8860(1) Å, b = 6.9164(1) Å, c = 10.6669(2) Å). The structure of the gallium compound had then solved by comparison with crystal structure of vanadium compound.

The examination of the systematic extinctions led to the space group Pnma (n° 62).

The atom positions were first fixed according to the structure of vanadium phase (vanadium was substituted to gallium on the 4a site) and then directly used as a starting model in our Rietveld refinement. The pattern matching procedures were performed with Fullprof2k using the WinPLOTR software package [20]. The geometric constraints used during the refinement were dGa–O = 2.00 ± 0.05 Å, dC–O = 1.25 ± 0.02 Å, dC–C = 1.42 ± 0.02 Å, O–C–C and C–C–C = 120.0 ± 0.02°, leading to a final reliability factors Rp = 0.0872 and Rwp = 0.1150. The corresponding Rietveld plot is reported on Fig. 2. Atomic coordinates and selected interatomic distances of MIL-61 (Ga) are given in Tables 1 and 2, respectively. The chemical formula deduced from the structure determination is Ga(OH)((HO2C)2–C6H4–(CO2)2)·0.5H2O and is in agreement with the elemental analysis (CNRS Analysis Center, Vernaison, France): Ga: obs.: 18% (calc.: 20%); C: obs.: 33% (calc.: 34%); H: obs.: 2.2% (calc.: 2.6%). Calculated density: 2.165 g·cm−3, measured density: 2.14(8) g·cm−3.

2.3. Solid state NMR

Solid-state 13C and 1H NMR characterization were performed on a Bruker Avance500 spectrometer with an 11.7 T magnetic field, in which these nuclei resonate at 125.8 and 500.1 MHz, respectively. An H/X 4 mm MAS probe-head and a classical ZrO2 rotor spun at 12.5 kHz were used for
Fig. 2. Final Rietveld plot of Ga(OH)(btec)·0.5H₂O (MIL-61). The open circles indicate observed data and the solid line represents the calculated data.

Table 1
Atomic coordinates of Ga(OH)(btec)·0.5H₂O (MIL-61)

<table>
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<tr>
<th>Atom</th>
<th>Wyckoff position</th>
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<th>y</th>
<th>z</th>
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<tr>
<td>Ga</td>
<td>4a</td>
<td>0</td>
<td>1/2</td>
<td>0</td>
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<td>8d</td>
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<td>0.58371(7)</td>
<td>0.03261(7)</td>
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<tr>
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<td>4c</td>
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<td>3/4</td>
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Table 2
Selected interatomic distances (Å) in Ga(OH)(btec)·0.5H₂O (MIL-61)

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<th>Atom–Atom</th>
<th>Distance (Å)</th>
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<tr>
<td>Ga–O(1)</td>
<td>2.028(6)</td>
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<tr>
<td>Ga–O(3)</td>
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<td>O(4)–C(8)</td>
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<td>1.262(1)</td>
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<td>O(6)–C(2)</td>
<td>1.319(1)</td>
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<tr>
<td>O(7)–C(2)</td>
<td>1.275(1)</td>
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<tr>
<td>C(1)–C(6)</td>
<td>1.496(9)</td>
</tr>
</tbody>
</table>

1H MAS experiment, and 42 kHz, 5.9 µs, 512 scans, and 10 s for the 13C{1H} MAS broadband decoupling experiment. Chemical shift reference was TMS for both 1H and 13C spectra.

3. Results and discussion

3.1. Structure description

The structure of Ga(OH)(btec)·0.5H₂O is similar to that of the previously reported vanadate MIL-61 [18]. It exhibits a complex three-dimensional hybrid framework built
Fig. 3. Projection along (a) [010], (b) [001] and (c) [101] of the structure of Ga(OH)(btec)·0.5H₂O (MIL-61).

Fig. 4. The interactions of carboxylic acid with (a) the inorganic chains through two carboxylate functions and with (b) the water molecule via hydrogen bond network in the structure of Ga(OH)(btec)·0.5H₂O (MIL-61).

The inorganic chains and the organic acids are arranged between each other in a way to form a relative dense structure (Fig. 3(a)). Inside the inorganic chains, each gallium atom is octahedrally coordinated with six Ga–O distances varying between 1.895(4) and 2.056(6) Å. Oxygen atoms [O(2)] trans-located in the gallium-centered octahedron correspond to hydroxyl functions, as is demonstrated by valence-bond calculations [21] of about 1.28. The connections between the GaO₄(OH)₂ octahedra occur via the OH functions, giving rise to infinite chains running along [010] (Fig. 3(b)). Furthermore, two consecutive octahedra in one chain are bridged by two carboxylate functions of two different organic linkers, inducing a strong tilting of the octahedra.
Along \( b \), the phenyl rings linked to two different chains are stacked within a distance of 4.67 Å, while two phenyl rings linked to the same chain are separated by 6.78 Å, preventing \( \pi-\pi \) interactions between each other (Fig. 3(c)). A particular feature of the organic molecules could be noted: over the four carboxylates grafted on one phenyl ring, two of them in 2,4 position participate in the three-dimensional structure by bridging octahedra of two different octahedral chains, whereas the two remaining in 1,5 position are terminal. Geometrically, the two latter protonated carboxylates are in the plane of the ring, whereas the two other ones deprotonated are perpendicularly disposed. It was possible to distinguish between them using FT-IR spectroscopy showing bands around 1200 and 1350 cm\(^{-1}\) for \( \nu_{C-O} \) of free non-bonded carboxylic acid groups (COOH) and around 1645 cm\(^{-1}\) due to \( \nu_{C=O} \) of bonded carboxylate groups (COO). Fine analysis of C–O distances confirms attribution of different kinds of carboxylate functions in pyromelilitic ligand (Fig. 4(a)). The two deprotonated linked functions (–COO–) in position 2,4 had short C–O distances of 1.251(8) and 1.258(7) Å, while the two other protonated non-bonded function (–COOH) in 1,5 position showed longer C–O distances of 1.319(1) and 1.262(1) Å. These later give rise to hydrogen bonds with water molecules occluded in the cavities of the framework in the special position 4c (Fig. 4(b)). Moreover, further interactions between water molecule and gallium-centered octahedral unit exist either through hydrogen atom of water and oxygen atom of gallium (\( O_{\text{w}} \cdots O_{\text{terminal}} = 2.902 \text{ to } 3.299 \) Å) or oxygen atom of water and hydrogen of \( \mu_2 \)-hydroxo (\( O_{\text{w}} \cdots O_{\text{bridged}} = 3.282 \) Å).

### 3.2. Solid state NMR

Ga(OH)(btec)-0.5H\(_2\)O (MIL-61) was subjected to \(^1\)H and \(^{13}\)C\(^{\{1\}H}\) decoupled NMR measurements. The \(^1\)H NMR spectrum is displayed in Fig. 5 and is composed of at least five overlapping signals. NMR parameters and assignment are given in Table 3. The signal at \( \delta = 4.3 \) ppm can be assigned to the Ga–OH–Ga \( \mu_2 \)-bridging hydroxides. Ga–OH groups generally resonate at lower frequency, around 0 to \(-1 \) ppm [22]. The shift toward lower shielding may be due to the implication of these protons in hydrogen bond network with the occluded water molecule. Typically, the peak at \( \delta = 5.5 \) ppm is attributable to water molecule of the structure. This resonance accounts for 15% of total NMR signals intensity, very close to the expected value 17% based on global chemical formula. The signal of the two aromatic protons of organic molecule is featured at \( \delta = 8.6 \) ppm with an intensity of 41% of total NMR signal as expected (theoretical 33%). Two distinct low-field signals at \( \delta = 10.8 \) ppm

<table>
<thead>
<tr>
<th>( \delta ) (ppm)</th>
<th>Experimental intensity(^a) (%)</th>
<th>Theoretical intensity(^b) (%)</th>
<th>Attribution</th>
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<tbody>
<tr>
<td>4.3</td>
<td>18</td>
<td>17</td>
<td>(-\text{OH})</td>
</tr>
<tr>
<td>5.5</td>
<td>15</td>
<td>17</td>
<td>( \text{H}_2\text{O})</td>
</tr>
<tr>
<td>8.6</td>
<td>41</td>
<td>33</td>
<td>aromatics</td>
</tr>
<tr>
<td>10.8</td>
<td>13</td>
<td>33</td>
<td>(-\text{COOH})</td>
</tr>
<tr>
<td>13.0</td>
<td>13</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Values from spectrum decomposition within estimated error of \( \pm 4\%\).

\(^b\) Expected values according to chemical formula.

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Fig. 5. Experimental \(^1\)H MAS NMR spectrum (top) of Ga(OH)(btec)-0.5H\(_2\)O (MIL-61) collected at a spinning speed of 30 kHz. The simulated spectrum and its decomposition are included (bottom) showing five components.
Fig. 6. $^{13}\text{C}[^1\text{H}]$ decoupled MAS NMR spectrum of Ga(OH)(btec)-0.5H$_2$O (MIL-61) acquired at a spinning speed of 12.5 kHz.

and 13.0 ppm are observed due to carboxylic acidic protons (–COOH) [13] indicating that some carboxylic acid groups are still protonated. According to quantification of these signals (13% + 13% = 26%) and by comparison to the theoretical amount of carboxylic acid (33% of proton), one can conclude that half of the carboxylic groups are protonated in good agreement with the structure determination. The existence of two different resonances for these carboxylic acid protons could account for two different local environments in the solid. This is consistent with different interaction types through hydrogen bonds as evidenced by the structure determination (Fig. 4). Fig. 6 displays the $^{13}\text{C}[^1\text{H}]$ decoupled NMR spectrum. The signals at $\delta = 123.3$, 142.3 and 145.2 ppm are attributable to aromatic carbons of the carboxylic acid molecule. Signals at lower field on one hand $\delta = 165.2$ ppm and on the other hand $\delta = 176.2$ and 174.7 ppm can be assigned to the carbons of the unprotonated carboxylate functions and protonated carboxylic acid functions respectively. Here again, we can distinguish between the two different carboxylic acid groups due to the different hydrogen bond networks.

3.3. Thermogravimetric analysis

The thermogravimetric analysis of Ga(OH)(btec)-0.5H$_2$O (under N$_2$, 3 °C·min$^{-1}$, TA Instrument 2050) was carried out in a temperature range from room to 600 °C (Fig. 7). Weight loss started around 200 °C and finished at 475 °C. A first event could be assigned to departure of free water molecules (obs.: 4.7%; calc.: 2.6%). The second weight loss happened in two steps and corresponds to the removal of pyromellitic acid molecules (obs.: 68.5%; calc.: 70.6%) during which decomposition occurred. The discrepancies between observed and calculated weight losses observed during the removal of both water and organic molecules are due to the overlapping of the two phenomena. Indeed, a perfect agreement between theoretical and experimental values (obs.: 73.2%; cal.: 73.2%) is found for the overall weight losses. At 600 °C, the XRD pattern of the residue corresponds to the gallium oxide Ga$_2$O$_3$.

4. Summary

The present study has reported the hydrothermal synthesis of a new gallium pyromellitate Ga(OH)(btec)-0.5H$_2$O (MIL-61). This solid possesses a three-dimensional gallium-btec framework, which encapsulates the water molecules. It is built up from the connection of pyromellitate ligands with
infinite straight chains of GaO$_4$(OH)$_2$ units. To the best of our knowledge, this phase is the first example of gallium carboxylate networks based on the linkage of btec moieties with the Ga–O–C cores. Other pyromellitates compounds however were observed using bivalent metals like iron [23], cobalt [24,25], copper [26] or cadmium [27].

References