SUPPORTING INFORMATION

**Title:** Re-Determination of the Crystal Structure of MIL-91(Al)

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S1 Methods

N, N′-piperazinebis(methylene phosphonic acid) was synthesised according to literature method. All other reagents and solvents were commercially available and used without further purification. Elemental analysis (C H N S) was performed on a EuroEA3000, using Sulfanilamide as the reference. Thermogravimetric measurements were performed under a stream of air (75 mL min^{-1}) using a Netsch STA-409CD instrument running, with data collected over the range 25 to 900°C and a heating rate of 4°C min^{-1}. For sorption experiments, 20-40 mg MIL-91(Al) were activated at 140°C for 12 hrs under reduced pressure (10^{-2} kPa). N2 and H2O sorption measurements were carried out using a BELSORP-max (BEL Japan Inc.). The surface area was determined with the BET method, for which the pressure range for application of the BET method was determined by a Rouquerol plot (end point at p/p0 = 0.0399). Pore volume was determined at p/p0 = 0.5. The IR spectra were recorded on a Bruker ALPHA-P FTIR spectrometer in the spectral range 4000–400 cm^{-1}. 
S2 Synthesis

N, N’-piperazinebismethyleneosphosphonic acid (40 mg, 0.15 mmol) and AlCl₃·6H₂O (17.6 mg, 0.073 mmol) were placed in Teflon® lined autoclave (V_max=2 ml) with deionised water (1 ml) to give a reaction concentration of 0.223 mol dm⁻³. The liner was then inserted into one of our in-house developed 24 reaction high-throughput multiclaves.[4] The reactor was slowly heated to 190°C over 12 hrs and the temperature was kept constant for 64 h, before the reactor was cooled to room temperature, again over 12 hours. The precipitate was filtered and washed with water. The final product was a colourless microcrystalline powder, consisting of clumps of needle shaped crystallites (14.5 mg, 0.039 mmol; yield 53 %, based on AlCl₃·6H₂O).

Elemental analysis gave C 18.85 % H 6.34 % N 7.12 %; expected for [Al(OH)(C₆H₁₄N₂P₂O₆)]·3H₂O: C 18.56 % H 5.97 % N 7.21 %.

S3 Thermogravimetric Analysis

[Graph showing thermogravimetric analysis]

Weight loss from 25 to 210°C corresponds to the loss of approximately three molecules of water per formula unit (observed 15.0 wt.%; expected 14.6 wt.%). From 210 °C to 280 °C is attributed to the dehydroxylation of the framework (observed -5.3 wt. %; expected -4.9 wt. %). Above 350°C the organic portion of the framework is lost (observed 32.6 wt.%; expected 30.3 wt.%, for C₆H₁₂N₂). Final product is thought to be a complex X-ray amorphous mixture of aluminium ortho- and metaphosphate (AlPO₄ and AlP₃O₉) with composition Al₂P₄O₁₃.
**Figure S1.** IR spectrum of MIL-91(Al).

\[ \text{IR } \tilde{\nu} \text{ (cm}^{-1}\text{)} = 3675 \text{ (w), 3375 (b), 3019 (w), 1674 (b), 1521 (w), 1473 (w), 1455 (w), 1442 (w), 1407 (w), 1394 (w), 1374 (w), 1333 (w), 1305 (w), 1266 (w) 1204 (w), 1133 (m), 1095 (s), 1057 (m), 1028 (m), 1010 (m), 977 (m), 961 (s), 935 (m), 889 (w), 850 (w), 832 (w), 810 (w), 770 (m), 736 (m), 673 (w), 648 (w), 620 (m), 581 (w), 558 (w), 548 (w), 519 (s), 490 (m), 431 (s), 418 (s).} \]

N.B. The sharp band at 3675 cm\(^{-1}\) can be assigned to the O-H stretch of the corner-shared hydroxyl groups.
S5 Crystallographic Methodology

A sample of MIL-91(Al) lightly ground before being loaded into a 0.7 mm borosilicate glass capillary tube. This was then mounted on the diffractometer at beamline I11, Diamond Light Source (Oxon., UK). Diffraction data were collected in a Debye-Scherrer geometry using the Multi-Crystal Analyser (MAC) detector with monochromatic synchrotron X-ray radiation ($\lambda = 0.825781\text{Å}$; calibrant: NIST SRM 640c). By collecting data with the MAC it was possible to measure a wide range of data (0-150° 2$\theta$) with a very high resolution (step size 0.001°). Data were collected for 30 mins on the same portion of the capillary; no appreciable beam-damage was observed.

For analysis, data in the range 3.4-44.4° 2$\theta$ were selected, as this range of data showed relatively well defined peaks with identifiable profiles. All data analysis was performed using the program TOPAS-Academic v5. Peaks were very carefully selected and indexing yielded a triclinic cell with a volume approximately half that of the reported monoclinic cell (Table S5.1). A Le Bail fit of this cell was then performed, with the data fitted to a Pseudo-Voigt peak shape. During the Le Bail fitting, it was found that some of the peaks show asymmetric broadening; this was fitted using the Stephens model implemented within TOPAS. The final Le Bail fit gave an $R_{wp} = 10.06\%$ (Table S5.1). Using the same peak profile functions and background, but with the reported monoclinic cell gave a significantly worse fit ($R_{wp} = 24.81\%$) (see Section S7 for detailed comparison).

| Literature Structure$^{[9]}$ | This work |
|----------------------------|-----------|
| Crystal System | Monoclinic | Triclinic |
| Space group | C2/m | P-1 |
| $a$ / Å | 18.859(9) | 6.920912(18) |
| $b$ / Å | 6.915(3) | 10.07905(3) |
| $c$ / Å | 11.256(6) | 11.27706(4) |
| $\alpha$ / ° | - | 90.2622(3) |
| $\beta$ / ° | 90.54(2) | 89.9121(3) |
| $\gamma$ / ° | - | 69.6855(3) |
| Volume / Å³ | 1467.8(13) | 737.705(4) |

A model for MIL-91(Al) with a triclinic symmetry was developed from the reported structure, using Materials Studio and PLATON.$^{[10,11]}$ The symmetry of the structure was first lowered and the disorder removed. Cell parameters and symmetry were then revised, using PLATON, and found to be in good
agreement with the cell parameters derived from the Le Bail fit. Finally the structure was geometry optimised.

The model was refined by the Rietveld method, using the peak function, background and cell derived from the Le Bail fit as starting model. Restraints were applied to all bonding distances and to some non-bonding distances (Table S5.2). Once the structure of the framework was well refined, water molecules (present as O atoms in the model) were deleted and after a couple of cycles of refinement, located by Fourier difference maps. It was found that a model including two disordered water molecules (O103 & O104), with a total occupancy of one O atom, gave an improved fit compared to a single fully occupied O atom.

**Table S5.2.** List of restraints applied to the model during Rietveld refinement.

| Bonding Distances            | Non-Bonding Distances             |
|------------------------------|-----------------------------------|
| Distance | Restraint ± ESD / Å | Distance | Restraint ± ESD / Å |
| Al-O     | 1.90±0.005          | O...O (P td.) | 2.53±0.01          |
| P-O      | 1.53±0.001          | O...C (P td.) | 2.78±0.01          |
| P-C      | 1.85±0.001          | N...N (x-ring) | 2.88±0.005         |
| C-N (ex. ring) | 1.52±0.001     | C...C (x-ring) | 2.88±0.005         |
| C-N (int. ring) | 1.50±0.001    | C-N (2nd neighbour) | 2.45±0.005        |
| C-C      | 1.50±0.001          | C-C (2nd neighbour) | 2.45±0.005        |

During the Rietveld refinement, the peak shape model was changed to use the full axial divergence model (rather than simple axial) to model the asymmetry of the first two peaks.\cite{12,13} In the final cycles of refinement, the isotropic ADPs (represented as beq in the CIF) were also refined: framework ADPs were constrained to refine as one group and water molecule ADPs as a second. The final refinement gave a good fit to the data ($R_{wp} = 9.22\%$; $\chi^2 = 4.599$ – Fig. S5.1).

The slightly high $R_{wp}$ reflects difficulties encountered in fitting the peak shape. Whilst the Stephens model fits isotropic strain within a crystal, the differences in the peak shape may indicate anisotropic strain. It was decided that as most peaks (excluding the (001) and the (010)) were well fitted and the $\chi^2$ is good, further modelling would be deleterious to the refinement as it would introduce additional free parameters that could mask structural data.
Fig. S5.1. Final Rietveld plots for the refinement of MIL-91(Al). ($R_{wp} = 9.22 \%$; $\chi^2 = 4.599$).
### S6  Summary of Crystallographic Results

#### Table S6. Crystallographic data for MIL-91(Al).

| Structural formula | [Al(OH)(H₂L)]·3H₂O# |
|--------------------|-----------------------|
| Moiety formula     | C₆H₁₅AlN₂O₇P₂, 3(H₂O) |
| Sum formula        | C₆H₂₁AlN₂O₁₀P₂        |
| Formula weight     | 370.17                |
| Calculated Density / g cm⁻³ | 1.666              |
| Space Group        | P-1                   |
| a / Å              | 6.921408(17)          |
| b / Å              | 10.05342(3)           |
| c / Å              | 11.27829(4)           |
| α / °              | 89.6820(4)            |
| β / °              | 89.9141(3)            |
| γ / °              | 70.0966(3)            |
| V /Å³              | 737.899(4)            |
| Z                  | 2                     |
| Diffractometer     | I11 / Diamond Light Source |
| Temperature        | 298                   |
| Wavelength / Å      | 0.825781              |
| No. Reflections    | 1221                  |
| No. Atoms          | 23                    |
| No. Restraints     | 52                    |
| \( R_p / \% \)     | 7.02                  |
| \( R_{wp} / \% \)  | 9.22                  |
| \( \chi^2 \)       | 4.599                 |
| \( R_{Bragg} / \% \)| 4.04                 |

# H₄L= N,N’-piperazinebis(methylene phosphonic acid) – C₆H₁₆N₂O₆P₂
Fig. S6.1. Asymmetric unit of MIL-91(Al); note the two symmetry independent half N,N’-piperazinebis(methylene phosphonate) linkers. Al atoms are located on special positions within the cell. Occupancy of the disordered O104 and O103 sites is indicated by filling of sphere. (Key: dark blue – Al; red – O; pink – P; pale blue – N; brown – C.

Fig. S6.2. View of MIL-91(Al) parallel to the a-axis, showing the water molecules in the channels. (Key – as Fig. S6.1; black box indicates the unit cell).
Fig. S6.3. View of MIL-91(Al) parallel to the $b$-axis, showing the structure of the chains and the connectivity between them. (Key – as Fig. S6.1; black box indicates the unit cell).
Comparison of Le Bail Fits of Reported $C2/m$ and New $P1,\bar{1}$ MIL-91(Al) Structures

| Reported Structure | Structure From This Work |
|--------------------|--------------------------|
| $C2/m$             | $P-1$                    |

The plots above illustrate the differences in the Le Bail fits over crucial regions of the diffraction data.

Peak profile (Pseudo-Voigt peak shape + Stephens anisotropic broadening$^{[8]}$) and background parameters were first refined for the triclinic cell to obtain good starting values. These were then

$\lambda = 0.825781 \text{ Å}$
used as a starting point for a refinement which included the unit cell and zero point of a) the monoclinic cell (results shown left) and b) the triclinic cell (results shown right) (N.B. for the monoclinic refinement, the Stephens model used was for monoclinic crystal systems). In the final cycles of refinement, all parameters were allowed to refine freely.

The Le Bail fit of the monoclinic cell gave a poor fit to the data ($R_{wp} = 24.81\%$) whilst the triclinic cell gave a much more acceptable fit ($R_{wp} = 10.06\%$). From the plots above, it is clear that there are indeed more peaks that can be fitted with a monoclinic model and therefore the triclinic unit cell which we propose in this work is the best candidate.
S8 Comparison of the Crystal Structures of Reported $C2/m$ and New $P\bar{1}$ MIL-91(Al)

| $C2/m$ | $P\bar{1}$ |
|--------|-----------|
| ![View parallel to $a$-axis](image1.png) | ![View parallel to $a$-axis](image2.png) |
| ![View parallel to $b$-axis](image3.png) | ![View parallel to $b$-axis](image4.png) |
Fig. S8.1. Comparison of the crystal structures of MIL-91(Al) in the literature monoclinic $C2/m$ cell\textsuperscript{[9]} (left) and the new triclinic $P-1$ cell reported in this work. Structurally there is very little difference between the two models, but crucially disorder has been removed in the new structure.

Fig. S8.2. Schematic of showing the two cells overlaid on top of one another. The monoclinic $C2/m$ cell of Serre et al. is shown in red and the new triclinic $P-1$ cell is shown in green. Note that to maintain the right-hand axis set, the orientation of the $c$-axis has changed by 180°.
Figure S9.1. Space filling model of one channel of MIL-91(Al), view along the $a$-axis. A sphere of 3.5 Å in diameter is added to demonstrate the pore size. O in red, N in blue, C in black, Al in grey and P in pink.

Figure S9.2 Comparison of the PXRD patterns of MIL-91(Al) as-synthesized (blue curve) and after the H$_2$O sorption measurements (red curve) with a simulated PXRD pattern (black curve).
S10 References

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