Structures and H₂ Adsorption Properties of Porous Scandium Metal–Organic Frameworks

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Abstract: Two new three-dimensional Sc^{III} metal-organic frameworks $\{[Sc_{3}O(L^{1})_{3}(H_{2}O)_{3}] \cdot Cl_{0.5}(OH)_{0.5}(DMF)_{4} (H_2O)_3$ (1) $(H_2L^1 = 1, 4$ -benzene-dicarboxvlic acid) and $\{[Sc_3O(L^2)_2 (H_2O)_3](OH)(H_2O)_5(DMF)\}_{\infty}$ (2) $(H_3L^2 = 1,3,5$ -tris(4-carboxyphenyl)benzene) have been synthesised and characterised. The structures of both 1 and 2 incorporate the trinuclear trigonal planar [Sc₃(O)(O₂CR)₆] building block featuring three Sc^{III} centres joined by a central μ_3 -O²⁻ donor. Each Sc^{III} centre is further bound by four oxygen donors from four different bridging carboxylate anions, and a molecule of water located *trans* to the μ_3 -O²⁻ donor completes the six coordination at the metal centre. Frameworks 1 and 2 show high thermal stability with retention of crystallinity up to 350 °C. The desolvated materials **1a** and **2a**, in which the solvent has been removed from the pores but with water or hydroxide remaining coordinated to Sc^{III}, show BET surface areas based upon N₂ uptake of 634 and 1233 m²g⁻¹, respectively, and pore volumes calculated from the maximum N₂ adsorption of $0.25 \text{ cm}^3\text{g}^{-1}$ and $0.62 \text{ cm}^3\text{g}^{-1}$, respectively. At 20 bar and 78 K, the H₂ isotherms for desolvated **1a** and **2a** con-

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firm 2.48 and 1.99 wt % total H₂ uptake, respectively. The isosteric heats of adsorption were estimated to be 5.25 and $2.59 \text{ kJ} \text{mol}^{-1}$ at zero surface coverage for 1a and 2a, respectively. Treatment of 2 with acetone followed by thermal desolvation in vacuo generated free metal coordination sites in a new material 2b. Framework 2b shows an enhanced BET surface area of $1511 \text{ m}^2 \text{g}^{-1}$ and a pore volume of $0.76 \text{ cm}^3 \text{g}^{-1}$, with improved H₂ uptake capacity and a higher heat of H₂ adsorption. At 20 bar, H₂ capacity increases from 1.99 wt% in 2a to 2.64 wt % for **2b**, and the H_2 adsorption enthalpy rises markedly from 2.59 to 6.90 kJ mol^{-1} .

Introduction

The development of coordination polymers in materials science, crystal engineering and supramolecular chemistry is a very timely area of research.^[1] The design and synthesis of such networks is driven by diverse potential applications in gas storage,^[2] catalysis,^[3] electrical conductivity,^[4] luminescence,^[5] magnetism^[6] and optics.^[7] Hydrogen has enormous potential as a sustainable, clean and efficient fuel.^[8] Thus, many industrial economies are investing in the hydrogen economy^[9] as a major contribution to sustainability and for use in the clean technologies of the future. There is, therefore, an enormous current interest in developing new metalorganic frameworks that show permanent porosity as H₂ storage materials.^[10] A very important parameter used to characterise this kind of material is the isosteric heat of adsorption,^[11] which describes the H₂ binding energy in porous materials. The typical values of heat adsorption for a metal-

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organic frameworks (at 78 K) are between 5 and 8 kJ mol⁻¹,^[12-15] but higher values of isosteric heat adsorption (15–20 kJ mol⁻¹) are required for a H₂ storage system^[16] that functions at room temperature and within a pressure range of 1.5–20 bar. In order to enhance the H₂ binding energy in these materials, strategies such as the formation of very narrow pores^[14,15,17] (in which overlapping potentials from two or more pore walls increases the binding energy between the H₂ and the framework), framework catenation/interpenetration^[18] and doping of frameworks with light electron-donating non-transition-metal centres to increase H₂ uptake^[19] have been undertaken. In particular, access to exposed metal sites can increase the affinity of H₂ through direct coordination to metal centres.^[12,20,21]

Most of the porous coordination framework polymers reported thus far have been based on divalent cations, commonly those of late-transition-metals such as Zn^{II}, Cu^{II} and Ni^{II}. In contrast, framework polymers derived from trivalent cations are less well known and are most commonly based upon Cr^{III} ,^[22,23] Sc^{III} ,^[24,25] $V^{III[26,27]}$ and Fe^{III} ,^[28] There is a growing interest in the use of Sc^{III} centres as components of porous frameworks because scandium is lighter than late divalent transitions metals, requires a higher ratio of ligands that contain only low-atomic-weight elements, and can also favour high coordination numbers.^[29] Relatively few examples of Sc^{III} coordination polymers have been reported in the literature.^[24,25,30–34] but notable examples include $[Sc_2(L^1)_3]$ (H₂ L¹=benzene-1,4-dicarboxylic acid),^[24,30] which exhibits ScO₆ octahedra linked to six other metal nodes through bridging carboxylates. This material has a pore volume of 0.29 cm^3g^{-1} and a H₂ uptake capacity of 1.4 wt % at 0.66 bar.^[24,30] Of direct relevance to the work reported herein, Dietzel and co-workers have synthesised^[33] the first example of a μ_3 -oxo bridged Sc^{III} framework [Sc₃O- $(H_2O)_3(L)_3X](DEF)_4$ (X = Cl, NO₃) (H₂L = benzene-2,5-dihydroxy-1,4-dicarboxylic acid), which was found to decompose at around 140 °C upon removal of the solvent molecules and showed no permanent porosity. Other related Sc^{III} frameworks based upon methylphosphonates,^[32] succinates,^[25,31] 1,5- and 2,6-naphthalenedisulfonate frameworks^[35] have also been reported and have been shown to be active catalysts for acetylation and oxidation reactions^[25,31] as well as selective bifunctional heterogeneous catalysts in the epoxidation of linalool and the oxidation of sulphides.^[35]

Binuclear $[M_2(O_2CR)_4]$ and tetranuclear $[M_4O(O_2CR)_6]$ clusters have been used as nodes in framework construction.^[36] In comparison, fewer examples of coordination polymers based on trinuclear clusters of the type $[M_3(\mu_3-O)-(O_2CR)_6]$ have been reported, although a range of metal centres have been incorporated to give μ_3 -oxo bridged trinuclear clusters of V^{III},^[26] Cr^{III},^[23,37] Fe^{III},^[28,38,39] In^{III},^[14,40] Al^{III},^[41] Ga^{III[42]} and Ni^{II[39]}. We were interested in developing the framework chemistry of Sc^{III} in parallel with our previous studies on the use of late-transition-metal centres as nodes in coordination polymer construction,^[43] and targeted the rare μ_3 -oxo [Sc₃O] fragment as a potential building block. Our approach to the synthesis of two Sc^{III} polymers (1 and 2) is based on templating the trinuclear [Sc₃(μ_3 -O)-(O₂CR)₆] building blocks, which have the potential to give products of high thermal stability. We have also investigated the importance and relevance of free metal coordination sites generated by solvent exchange followed by thermal treatment.

Results and Discussion

Synthesis and Structure

Solvothermal reaction of ScCl₃•*x*H₂O with benzene-1,4-dicarboxylic acid (H₂L¹: Scheme 1) in a slightly acidified mixture of *N*,*N*'-dimethylformamide, 1,4-dioxane and water afforded {[Sc₃O(L¹)₃(H₂O)₃]•Cl_{0.5}(OH)_{0.5}(DMF)₄(H₂O)₃]_{∞} (**1**). ScCl₃•*x*H₂O and 1,3,5-tris(4-carboxyphenyl)benzene (H₃L²: Scheme 1) in acidified mixture of *N*,*N*'-dimethylformamide, tetrahydrofuran, dichloromethane and water under solvothermal conditions produced {[Sc₃O(L²)₂(H₂O)₃](OH)-(H₂O)₅(DMF)}_{∞} (**2**).



Scheme 1. H_2L^1 (1,4-benzene-dicarboxylic acid) and H_3L^2 (1,3,5-tris(4-carboxyphenyl)benzene).

A single-crystal X-ray structural determination confirms that 1 crystallises in the hexagonal space group $P6_3/mmc$, and has a structure based around the trinuclear building block $[Sc_3(O)(O_2CR)_6]$ (Figure 1 a and c), two of which are present in each unit cell. In each $[Sc_3(O)(O_2CR)_6]$ unit, three Sc^{III} centres are joined by a central μ_3 -oxygen atom [Sc-O 2.0254(8) Å] and the unit adopts a trigonal planar geometry and occupies a site of crystallographic D_{3h} symmetry. Each pair of centres is bridged by two carboxylate groups such that each metal centre is coordinated by four oxygen donors from different anions, and a molecule of water is located *trans* to the μ_3 -oxygen atom completing the Sc^{III} coordination sphere. Although this coordination is approximately octahedral, the metal occupies a site of lower crystallographic symmetry $(C_{2\nu})$. The main characteristic of the $[Sc_3(O)(O_2CR)_6]$ building block is the junction of the three octahedra by sharing a µ3-oxygen atom (Figure 1b). Each trinuclear cluster is connected to six neighbouring clusters through six benzene-1,4-dicarboxylates, and each trinuclear cluster $[Sc_3(O)(O_2CR)_6]$ can be viewed as a node linked to six nearby cluster nodes. Thus, the framework exhibits a three-dimensional network structure of 4966 topology incor-



Figure 1. a) Six-coordination of three scandium centres in approximately octahedral geometry; b) polyhedral representation of the three octahedra sharing a μ_3 -oxygen atom; c) trinuclear building block of **1** showing the ligand ($[L^1]^{2-}$) coordinated to the three scandium centres; d) trinuclear building block of **2**, which shows the ligand ($[L^2]^{3-}$) coordinated to the three scandium centres.

porating pores of approximately 7.6 Å diameter (Figure 2a) as calculated from the crystal structure. This value is in good agreement with the value of 8.0 Å estimated from the N_2 isotherm (see below). The channels are connected by narrow windows of approximately 3.5 Å diameter (Figure 2b). The precise locations of Cl⁻ and OH⁻ within the structure could not be determined by single-crystal X-ray diffraction, but the presence of Cl⁻ was confirmed by X-ray photoelectron spectroscopy (XPS).



Figure 2. a) View of the three-dimensional framework **1** along the *c* axis, which shows the channels of the structure; b) view of **1** along the *b* axis, which shows the windows that connect the framework channels (Sc = blue, O = red and C black; H atoms are omitted for clarity).

The structure of **2**, solved by single-crystal X-ray methods, crystallises in the hexagonal space group $P\bar{6}2c$ and, as for **1**, is based around the trinuclear cluster node $[Sc_3(O)(O_2CR)_6]$

(Figure 1 a and d). Three Sc^{III} centres are joined by a central μ_3 -oxygen atom, with Sc–O bond lengths in the range 1.991(3)–2.038(5) Å, and they adopt a trigonal planar geometry on a site of crystallographic C_s symmetry. Each Sc^{III} centre is octahedrally bound to six oxygen atoms from four different carboxylate groups, and a molecule of water is located *trans* to the μ_3 -oxygen atom. Each trinuclear building block is connected to twelve neighbouring building blocks through six ligands $[L^2]^{3-}$, and the pore diameter of this framework calculated from the crystal structure is approximately 23 Å (Figure 3a and b). The precise locations of



Figure 3. a) View of the three-dimensional framework 2 along the c axis, which shows the channels of the structure; b) space-filling view along the crystallographic c axis for 2 (Sc=blue, O=red and C=black and H= grey).

 OH^- within the structure could not be determined by single-crystal X-ray diffraction, but the presence of OH^- was confirmed by elemental analysis and XPS. Although the definition of protonation states of bound and in-pore H₂O, OH^- and O^{2-} moieties can be problematic in this type of system (see below), bond valence sum analysis confirms that the trinuclear cluster in **1** and **2** comprises of Sc^{III} centres with a central μ_3 -O²⁻ donor (see the Supplementary Information), and the terminal Sc–O bond lengths, 2.102(4) Å for **1**, and 2.137(7) and 2.155(5) Å for **2**, are consistent with coordinated H₂O.^[33,44]

Thermogravimetric analysis of 1 and 2 under N_2 shows one main, continuous, weight loss of 21 % (1) or 16 % (2) over temperature ranges of 25–250 °C and 25–340 °C, respectively. Whereas compound 1 starts to decompose at 490 °C, 2 reaches a plateau above 340 °C with the structure decomposing at 520 °C, a very high decomposition temperature for a metal–organic hybrid material. In situ variable-temperature powder X-ray diffraction (PXRD) measurements on samples of 1 and 2 held under vacuum confirmed the retention of crystallinity and overall structure of the frameworks up to 350 °C, with a good fit observed between the experimental PXRD data and that calculated from the single-crystal data.

In order to establish the fate of the water molecules within these materials, FTIR spectra were recorded over a range of temperatures under a flow of He gas. The FTIR spectrum of 1 at 25 °C (Figure 4a) shows a broad absorption band at 3490 cm^{-1} , confirming the presence of water at room temperature. A slight decrease in the intensity of this



Figure 4. a) FTIR spectra of 1 at various temperatures (under He flow); b) FTIR difference spectra of 1, which shows the peak attributed to coordinated water/hydroxide.

band is observed on raising the temperature from 25 to 50 °C under a flow of He gas, and a significant reduction in the intensity is observed on heating to 100°C. At 350°C the band has almost entirely disappeared, indicating the loss of nearly all of the water from the framework. We were unable to distinguish the sharp peak in the 3400–3700 cm⁻¹ region, characteristic of coordinated water/hydroxide from the intense broad band produced by uncoordinated water by means of conventional FTIR spectroscopy (Figure 4a). Therefore, difference spectroscopy was used to extract information from changes in intensities of overlapping bands. Thus, plotting differences between spectra at two temperatures (Figure 4b) allows differentiation of the two contributions. A sharp peak at 3680 cm⁻¹ attributed to coordinated water or hydroxide is discernible in the difference spectrum. Definitive assignment of the sharp peak at 3680 cm⁻¹ to either bound water or hydroxide was problematic^[33,44,45] in this case owing to overlapping bands in the 1600 cm^{-1} region from strong carboxylate stretches masking any distinctive H-O-H bending mode. At temperatures below 250 °C, the broad band at 3490 cm⁻¹ that is characteristic of

free water was observed, indicating that only uncoordinated molecules are removed from the framework on heating.

The free solvent molecules in the pores in **1** can be readily exchanged for other organic solvents such as acetone and this promotes accessibility to solvent-free frameworks after appropriate thermal treatment. The FTIR spectrum of the acetone-exchanged sample **1** under a He flow clearly showed the two relevant features: the broad absorption band assigned to uncoordinated water and the sharp peak assigned to coordinated water/hydroxide. At 25 °C the FTIR spectrum of the acetone-exchanged sample **1** (Figure 5)



Figure 5. FTIR spectra of the acetone-exchanged sample **1** at various temperatures under He flow, which shows the peak attributed to coordinated water/hydroxide.

showed a broad absorption band at 3490 cm^{-1} , confirming the presence of uncoordinated water in the framework. A significant decrease in the intensity of this band is observed on increasing the temperature from 25 to 50 °C. At 100 °C the band is lost from the spectra, indicating the removal of free water from the framework but with retention of the characteristic sharp peak at 3680 cm⁻¹ that is assigned to metal-coordinated water or hydroxide (Figure 5). Between room temperature and 350 °C this peak is retained in the spectra, suggesting that the coordinated water is not removed from the framework under these conditions and remains bound to Sc^{III}.

FTIR spectra of **2** at different temperatures were measured under a He flow. At 25 °C the broad absorption band at 3410 cm^{-1} that is characteristic of uncoordinated water was observed, which was accompanied by a peak at 3680 cm^{-1} (Figure 6). A continuous decrease in the intensity of the band at 3410 cm^{-1} is observed on raising the temperature from 25 to 200 °C, suggesting the loss of free water from the framework; meanwhile the intensity of the sharp peak at 3680 cm^{-1} remains unchanged. Upon increasing the temperature from 200 to 250 °C, the band at 3410 cm^{-1} is completely lost from the spectra, indicating removal of all of the uncoordinated water from the framework pores. Interestingly, and in contrast to compound **1**, the sharp peak at



Figure 6. FTIR spectra of **2** at various temperatures under He flow showing the peak attributed to coordinated water/hydroxide.

 3680 cm^{-1} is also lost from the spectra. On heating the sample from 250 up to 350 °C there is no further significant change in the spectra. Similar changes in the IR spectrum of the acetone-exchanged sample **2** (Figure 7) are observed



Figure 7. FTIR spectra of the acetone-exchanged sample **2** at various temperatures under He flow showing the peak attributed to coordinated water/hydroxide.

with removal of uncoordinated water by 150° C and coordinated water by 250° C. Thus, the FTIR results suggest that in the acetone-exchanged sample **1** it is possible to remove the uncoordinated water at 100° C and the coordinated water/hydroxide remains bound to Sc^{III} even at 350° C. However, in the acetone-exchanged sample **2** the uncoordinated water is removed at 150° C and the coordinated water is removed at 250° C.

A range of experiments was conducted on the desolvation of **1** and **2** under a range of conditions (various desolvation and activation temperatures and times) to optimise the porosity of the resultant materials **1a**, **2a** and **2b**. Treatment of **1** and **2** with acetone for 96 h followed by degassing at 170 °C and 10^{-10} bar for 12 h gave the fully desolvated materials **1a** and **2a** that retained coordinated water with optimised porosity. Acetone exchange of a sample **2** for 96 h followed by degassing at 250 °C and 10^{-10} bar for 12 h afforded the fully desolvated material **2b** with coordinated water/hydoxide removed. Heating of **1** and **2** in vacuo without solvent exchange afforded materials of lower apparent porosity that had lower gas-uptake capacity, possibly due to framework degradation.

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Gas adsorption analysis

Both N₂ adsorption analyses for 1a and 2a show typical Type I isotherm characteristics of microporous materials, which verifies the retention of the microporosity on removal of free solvents within the framework. The observed hysteresis loop in the isotherm for **1a** (Figure 8a) with a step in the profile for N₂ adsorption-desorption is evidence for a kinetic trap consistent with the charged nature of the microporous framework that is modulated by the presence of anions in the pores.^[46] The overall shape of the isotherm plot for 2a (Figure 8b) suggests a two-step adsorption although the N_2 adsorption analysis shows a Type I isotherm. Non-local density functional theory (NLDFT) analysis of the isotherm data for 2a (Figure 8c) confirms a pore diameter of 23.3 Å, consistent with the value determined from the crystal structure of 2. The Brunauer-Emmett-Teller (BET) surface areas and pore volumes calculated from the maximum N₂ adsorption for **1a** and **2a** were estimated to be $634 \text{ m}^2 \text{g}^{-1}/0.25 \text{ cm}^3 \text{g}^{-1}$ and $1233 \text{ m}^2 \text{g}^{-1}/0.62 \text{ cm}^3 \text{g}^{-1}$, respectively.

Gravimetric H₂ adsorption isotherms were measured for these materials from 0–20 bar at 78 K and 88 K (Table 1). All data were strictly corrected for the buoyancy of the system, samples and absorbates. All H₂ sorption isotherms showed good reversibility characteristic of microporous materials (Figure 8d, e and f). The values for the total H₂ uptake for the samples **1a** and **2a** are 2.48 and 1.99 wt %, respectively, at 20 bar. Significantly, solvent exchange represents a fundamental treatment step to enable formation of a fully solvent-free material. Materials **1** and **2** that were prepared without acetone exchange but with degassing at 170 °C and 10⁻¹⁰ bar for 36 h gave lower overall total H₂ uptakes of 1.62 and 1.33 wt %, respectively, at 20 bar, confirming the importance of acetone-exchange treatment prior to any gas-adsorption experiment.

The H₂ adsorption enthalpy was determined by recording isotherms at 78 and 88 K from 0–20 bar, and the data were analysed by using a virial-type equation.^[47] The isosteric heats of adsorption were estimated to be 5.25 and 2.59 kJ mol^{-1} at zero surface coverage for **1a** and **2a**, respectively, (Figure 9). These values decrease with increasing H₂ loading as expected. These are relatively low values relative to the systems that incorporate free metal coordination sites in which interaction between H₂ and metal centres can be maximised.^[11,21] For sample **2a** the isosteric heat of adsorption is even lower than **1a** owing to the large pore size of **2a** (≈ 23 Å); thus, the overall interaction between H₂ and the



Figure 8. a) N_2 adsorption isotherm and pore-size distribution for compound **1a**; b) N_2 adsorption isotherms for compounds **2a** and **2b**, respectively; c) pore-size distribution for compounds **2a** and **2b**; d) H_2 adsorption isotherms up to 20 bar at 78 and 88 K for **1a**; e) H_2 adsorption isotherms up to 20 bar at 78 and 88 K for **2a**; f) H_2 adsorption isotherms up to 20 bar at 78 and 88 K for **2a**; f) H_2 adsorption isotherms up to 20 bar at 78 and 88 K for **2b**.

Table 1. Gas-adsorption data for 1a, 2a and 2b.

	1a	2a	2 b
free metal coordination sites	no	no	yes
pore diameter [Å]	8.0	23.3	25.8
pore volume [cm ³ g ⁻¹]	0.25	0.62	0.76
BET surface area [m ² g ⁻¹]	634	1233	1511
H ₂ at 78 K and 1 bar [wt%]	0.94	0.91	1.01
H ₂ at 78 K and 20 bar [wt%]	2.44	1.99	2.64
Heat of adsorption [kJ mol ⁻¹]	5.25	2.59	6.90

pore are concluded to be weaker in 2a. Sun et al. have shown^[48] by using ab initio calculations based on DFT that a

high binding energy between H_2 and a vacant site on Sc^{III} would be expected within a porous hybrid solid. Taking the reverse argument, the relatively low value of the isosteric heat for H_2 adsorption in **1a** is consistent with the absence of free metal coordination sites supported by in situ infrared spectroscopy measurements, which confirmed the retention of the coordinated water/hydroxide at the metal site when the sample is heated up to 350 °C.

The shape of the isotherm for **2b** (Figure 8b) shows a two-step adsorption although, like the N_2 isotherm for **2a**, the N_2 adsorption analysis shows a Type I isotherm. NLDFT analysis for **2b** shows a pore diameter of 25.8 Å. The BET



Figure 9. Variation of adsorption enthalpy at low loading of H_2 for **1a** (red), **2a** (black) and **2b** (blue).

surface area and pore volume for 2b were estimated to be $1511 \text{ m}^2\text{g}^{-1}$ and $0.76 \text{ cm}^3\text{g}^{-1}$, respectively. Gravimetric H₂ adsorption data were recorded on 2b (Figure 8 f) over the range 0-20 bar at 78 K to give a total H₂ uptake of 2.64 wt% at 20 bar with a heat of adsorption^[47] of 6.90 kJmol^{-1} (Figure 9). Thus, the BET surface area and the pore volume are enhanced on going from 2a to 2b (i.e., on removal of coordinated water) from 1233 $m^2 g^{-1}/0.62 c m^3 g^{-1}$ and $1511 \text{ m}^2\text{g}^{-1}/0.76 \text{ cm}^3\text{g}^{-1}$, respectively. Also, the H₂ adsorption isotherms at 78 K show a corresponding improvement in total storage capacity on going from 2a to 2b. At 20 bar, H₂ capacity increases by one quarter from 1.99 wt % to 2.64 wt%, and the H₂ adsorption enthalpy also increases from 2.59 to 6.90 kJ mol⁻¹. Thus, from the IR analyses and the N₂ and H₂ adsorption data, the generation of free metal coordination sites on 2 after an appropriate solvation and thermal treatment provides a material with higher surface area, pore volume, H_2 uptake and H_2 heat of adsorption.

Conclusion

We have synthesised two Sc^{III} metal–organic frameworks incorporating the same trinuclear $[Sc_3(O)(O_2CR)_6]$ building block. This work represents the first examples of the use of a μ_3 -oxo bridged trinuclear Sc^{III} building block to construct frameworks that exhibit permanent porosity and H₂ adsorption properties. After an appropriate thermal treatment on the acetone-exchanged sample **2**, the generation of free metal coordination sites has been achieved thus enhancing H₂ uptake and heat of adsorption. Although **1** and **2** are based upon the same metal cluster, only in the case of framework **2** is it possible, in our hands, to access free metal coordination sites. We suggest that this is linked to the difference in pore size between the two frameworks and the more hydrophobic environment within framework **2**.

Experimental Section

Synthesis of H_3L^2 : 1,3,5-Tribromobenzene (1.00 g, 3.1 mmol), 4-ethoxycarbonylphenylboronic acid (2.22 g, 11.4 mmol) and K_3PO_4 (5.06 g, 23.8 mmol) were mixed in 1,4-dioxane (80 mL) and the mixture was degassed under argon for 10 min. [Pd(PPh_3)_4] (0.03 g, 0.031 mmol) was added to the reaction mixture with stirring and the mixture was heated to 85 °C for 4 days under argon. The solution was evaporated to dryness and the residue was extracted with chloroform. The final product H₃L was obtained by hydrolysing the crude product with 2 M aqueous NaOH, followed by acidification with concentrated HCl (1.18 g, 85 %). ¹H NMR (DMSO, 300.13 MHz, 298 K): δ =8.05 (6H, d; Ar-H), 7.78 (6H, d; Ar-H), 7.57 ppm(3H, s; Ar-H); ¹³C NMR (DMSO, 300.13 MHz, 298 K): δ = 169.1, 140.9, 136.7, 129.4, 127.7, 125.1 ppm; ¹³C NMR changed to 1 d.p., MS (ESI⁻): *m*/z: 437.1037 [*M*-H]⁺; elemental analysis calcd (%) for C₂₇H₁₈O₆: C 73.97; H 4.14; found: C 74.06; H 4.56.

Synthesis of 1: Scandium trichloride hydrate (0.065 g, 0.429 mmol) and benzene-1,4-dicarboxylic acid (0.020 g, 0.120 mmol) were mixed in *N*,*N*⁻ dimethylformamide (7.50 mL), 1,4-dioxane (3.75 mL), water (3.75 mL) and hydrochloric acid (36.5%, 2 drops) and sealed in a pressure tube. The tube was heated to 80 °C in an oil bath and then maintained at this temperature for 3 days. Finally the tube was cooled to room temperature over a period of 12 h. The colourless crystalline product was separated by filtration, washed with DMF (5.00 mL) and dried briefly in air (60% yield based on the ligand). Elemental analytical data corresponds to {[Sc₃O(L¹)₃(H₂O)₃].Cl_{0.5}OH_{0.5}(C₃H₇NO)₄(H₂O)₃]_∞: elemental analysis calcd (%) for M_r =1069.93: C 40.07; H 4.86; N 5.19; found: C 39.57; H 4.11; N 5.42%.

Synthesis of 2: Scandium trichloride hydrate (0.027 g, 0.135 mmol) and H₃L (0.020 g, 0.045 mmol) were mixed and dispersed in a mixture of dimethylformamide (3.0 mL), tetrahydrofuran (4.0 mL), dichloromethane (3.0 mL), water (3.0 mL) and concentrated nitric acid (68%, 3 drops). The reaction mixture was sealed and heated in a pressure tube to 120 °C for 48 h. The tube was cooled to room temperature over a period of 12 h. The colourless crystalline product was separated by filtration, washed with DMF (5.00 mL) and dried briefly in air (71% yield based on the ligand). Elemental analytical data corresponds to {[Sc₃O(L)₂(H₂O)₃]OH-(H₂O)₅(DMF)]_∞: elemental analysis calcd (%) for M_r =1254.88: C 54.51; H 4.33; N 1.12; found: C 54.87; H 4.78; N 1.15%.

X-ray crystallography: Intensity data for **1** were collected at 150(2) K on a Bruker SMART APEX CCD area-detector diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation. A colourless crystal was mounted in a film of Fomblin YR1800 perfluoropolyether (Lancaster) on a dualstage glass fibre immediately after removal from the mother liquid.

Crystal data for 1: $Sc_3O_{23.5}C_{36}H_{52.5}Cl_{0.5}N_4$; $M_r = 1069.93$; hexagonal; space group $P6_3/mmc$ (No. 194); a=b=14.056(2), c=18.099(4) Å; V=3096.8(9) Å³; Z=2; $D_{calcd}=1.147 \text{ g cm}^{-3}$; $\mu=0.407 \text{ mm}^{-1}$; of 18126 reflections collected, 1382 were independent with $R_{int} = 0.121$ and 1084 reflections with $[I > 2\sigma(I)]$ and final $R_1 [I > 2\sigma(I)] = 0.0592$; wR_2 (all data) = 0.158; goodness of fit=0.96. The structure was solved by direct methods and subsequent difference Fourier synthesis, and was refined by using the SHELXTL software package.^[49] The ligand H atoms were placed in idealised positions and refined by using a riding model. The H atoms of the coordinated H₂O molecules were located in a difference Fourier map. It was not possible to localise either chloride anions (derived from the starting material, ScCl₃·xH₂O) or hydroxide anions, although their presence is required to achieve charge neutrality. PLATON/SQUEEZE^[50] was used to calculate the diffraction contributions of the solvent molecules in order to produce a set of solvent-free diffraction intensities. The final formula was calculated from the SQUEEZE^[50] results combined with elemental analysis and XPS data. Diffraction data for 2 were collected at 120(2) K on Beamline I19 of the synchrotron at the Diamond Light Source using a Rigaku Saturn 724+ area-detector diffractometer: a colourless crystal was mounted in a loop by using Fomblin after removal from the mother liquid.

Crystal data for **2**: Sc₃O₂₃C₅₇H₅₄N, MW = 1254.88; hexagonal; space group $P\bar{6}2c$ (No. 190); a=b=31.470(4), c=16.843(3) Å; V=14446(4) Å³; Z=6;

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 $D_{\text{calcd}} = 0.865 \text{ g cm}^{-3}$; $\mu = 0.255 \text{ mm}^{-1}$; of 26384 reflections collected, 8207 were independent with $R_{int} = 0.120$ and 5027 reflections with $[I > 2\sigma(I)]$ and final R_1 [$I > 2\sigma(I)$]=0.0852; wR_2 (all data)=0.215, goodness of fit= 1.004. The details for data collection are included are included in CIF files in Supplementary Information. The structure was solved by direct methods and developed by difference Fourier techniques by using the SHELXTL software package.[47] The H atoms on the ligand were placed in idealised positions and were refined by using a riding model. It was not possible to localise any hydroxide anions, although their presence is required to achieve charge neutrality. We employed PLATON/ SQUEEZE^[50] to calculate the contribution to the diffraction from the solvent molecules and thereby produced a set of solvent-free diffraction intensities. The final formula was calculated from the SQUEEZE^[50] results combined with elemental analysis and XPS data. CCDC-769527 (1) and 769528 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

Gas adsorption measurements: Hydrogen and nitrogen absorption was measured in a Hiden Isochema Intelligent Gravimetric Analyser (IGA-003), which is an ultra-high-vacuum, clean instrument with a diaphragm and turbo pumping system, and is equipped with a micro-gram balance, and 2 mbar, 100 mbar and 20 bar pressure transducers. A liquid nitrogen Dewar vessel was employed for measurements at low temperature. IG-ASwin systems software v.1.03.143 (Hiden Isochema, 2004) were used to fit all isotherm data points by using a linear driving force model when >98% equilibration had been reached. All changes in the sample weight were corrected for buoyancy effects. Hydrogen was purified by using calcium aluminosilicate and activated carbon adsorbents in order to remove impurities and trace amounts of water.

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