A microporous scandium terephthalate, $Sc_2(O_2CC_6H_4CO_2)_3$, with high thermal stability†

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A scandium terephthalate with isolated ScO_6 octahedra and fully-linked carboxylate groups is prepared hydrothermally and possesses a novel hybrid framework structure with high thermal stability and a pore volume for N_2 adsorption of 0.26 cm^3 g^{-1} at 77 K.

Remarkable progress has been made in the synthesis of porous metal di- and tricarboxylates with giant pores and well-defined, thermally stable frameworks.[1,2] This opens up exciting possibilities in the adsorption, storage and separation of molecules with free diameters of up to 10 Å that are only just beginning to be explored. More traditionally, though, many important applications of adsorption involve the uptake and separation of small gas molecules (such as N_2, O_2, CH_4 and CO_2)[3] and there is also great current interest in the use of porous solids for hydrogen storage[4,5] and purification[6] as an important technological requirement for implementation of the hydrogen economy, so that the search for porous solids with small pores and stable frameworks should not be neglected. That small pore framework solids with walls made predominantly of aromatic rings can be of significance in this area has recently been illustrated by Sozzani et al. for a porous van der Waals crystal.[7] Here we describe a scandium terephthalate framework, prepared by hydrothermal methods, that demonstrates significant microporosity for small molecules and possesses remarkable thermal stability. The results complement and extend the recent reports of open framework solids comprising sulfates,[8] phosphates[9] and phosphonates[10] of scandium. The current interest in scandium as a component of open frameworks stems from its increased availability at reasonable cost and its chemical similarities (in terms of ionic radius, coordination and acid/base behaviour) to elements such as aluminium, chromium and iron that have been found to form stable open frameworks of phosphates and, more recently, carboxylates.[2,11,12] Scandium carboxylates have been observed to possess significant Lewis acidity in catalytic reactions.[13]

The title compound was prepared hydrothermally by the reaction of scandium nitrate and terephthalic acid.‡ It comprises a remarkable three-dimensionally connected framework (Fig. 1) that is made up of chains of isolated ScO_6 octahedra running parallel to [100]. Each ScO_6 octahedron in the chain is linked to those above and below by three carboxylate units, each of which is monodentate to two scandium ions along the a axis. The mean Sc–O bond length is 2.07(2) Å. Each chain is linked to six adjacent chains through terephthalate units: two of the six sets of terephthalate linkers (parallel to the b axis) connect to chains of ScO_6 octahedra at the same fractional coordinate along the a axis (Fig. 2, top), the other four (parallel to planes of the form {011}) connect alternately to chains at higher and lower coordinates in x (Fig. 2, bottom).

The framework includes small channels along the a axis that have triangular cross sections: the triangle is made up of the projection (parallel to the plane) of terephthalate units linking chains of ScO_6 octahedra. These channels are linked perpendicularly through small windows between adjacent aromatic rings. The channels have free diameters (taking van der Waals radii of C to be 1.7 Å) of around 3 Å, although the staggered arrangement of the terephthalic linkers makes accurate measurement difficult. The windows between aromatic rings stacked along a, between adjacent channels, calculated from the positions of the terepthalate groups determined by single crystal X-ray diffraction, are small (ca. 2 Å, see Figs. 2a and b). Four of the six sets of terephthalate linkers from any one chain of ScO_6 octahedra join to adjacent chains of octahedra at different levels, as described previously in Fig. 2b, so that it is not possible for this structure to show 'iso-reticulation'. That is, the terephthalate could not straightforwardly be replaced by longer linear dicarboxylic acids, such as 4,4′-biphenyldicarboxylic acid, as has been demonstrated to be possible to give larger pore versions of the zinc terephthalate, MOF-5.[14]
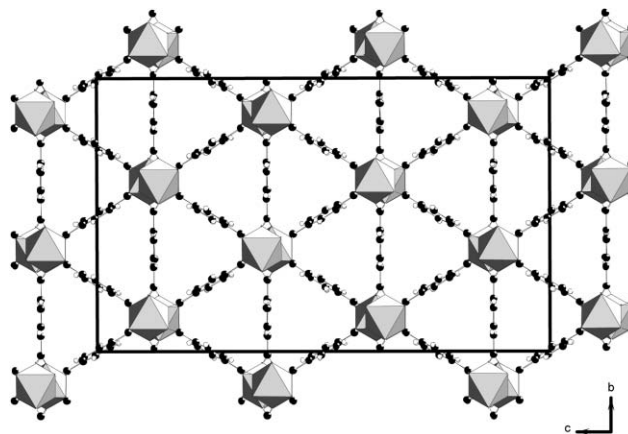
[a]School of Chemistry, University of St. Andrews, St. Andrews, Fife, UK KY16 9ST. E-mail: paw2@st-andrews.ac.uk; Fax: 1334 463808; Tel: 1334 463793
[b]Institut Lavoisier, UMR CNRS 8637, University of Versailles-St. Quentin-en-Yvelines, 45, Avenue des Etats-Unis, 78035, Versailles, France

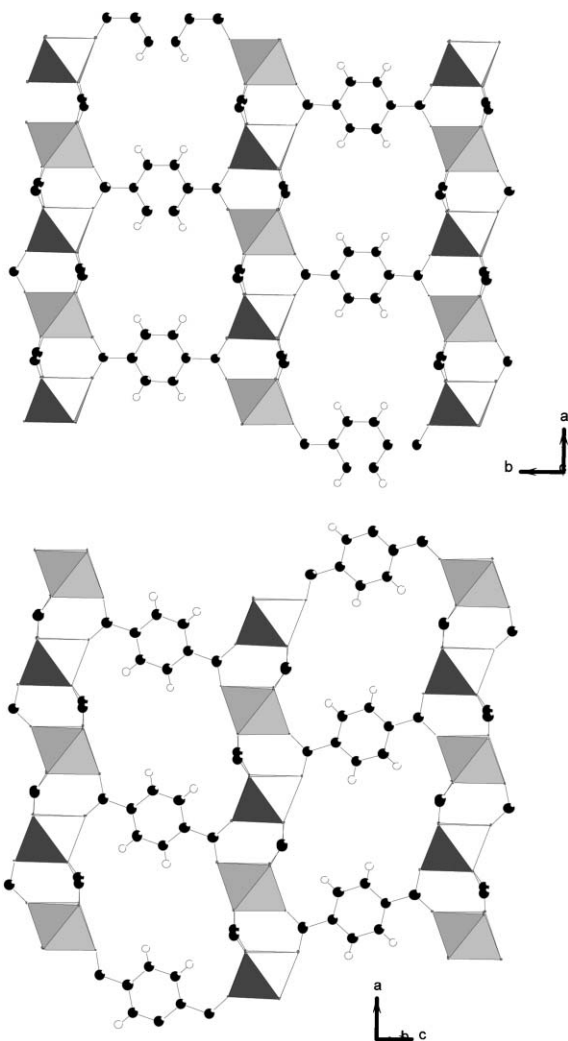† Electronic supplementary information (ESI) available: matched X-ray powder pattern. See http://dx.doi.org/10.1039/b506677h

Fig. 1 The framework compound $Sc_2(O_2CC_6H_4CO_2)_3$, viewed down the a axis. ScO_6 units are represented as gray octahedra.

Fig. 2 The framework compound $Sc_2(O_2CC_6H_4CO_2)_3$, viewed along the b axis (top) or down the c axis (bottom). ScO_6 units are represented as gray octahedra.

Fig. 3 (Top) Thermogravimetric analysis of as-prepared $Sc_2(O_2CC_6H_4CO_2)_3$ and a sample previously heated at 275 °C to remove free terephthalic acid. (Bottom) X-Ray thermodiffractometry of as-prepared $Sc_2(O_2CC_6H_4CO_2)_3$.

Fig. 4 *In situ* X-ray thermodiffraction (Co K_α, λ = 1.790 Å) indicates that the solid remains crystalline in air up to 400 °C.

Fig. 5 N_2 adsorption isotherm on $Sc_2(O_2CC_6H_4CO_2)_3$ at 77 K.

Negligible electron density attributable to included water was observed by the single crystal diffraction measurement, although TGA in an oxygen atmosphere (Fig. 3) showed an initial weight loss of 5%, attributed to loss of very weakly bound water. The TGA shows a further weight loss of around 5% up to 275 °C, due to the loss of free terephthalic acid. After this, the material shows slow weight loss until a major weight loss (*ca.* 60%) occurs at around 500 °C as the carboxylate decomposes. A sample heated at 275 °C overnight to remove free acid and subsequently re-examined by TGA shows a single weight loss at around 475 °C (expected weight loss to leave scandium oxide, 76 wt%; measured loss to 600 °C, 74%). *In situ* X-ray thermodiffraction under air (Fig. 4) indicates that the solid remains crystalline up to 400 °C, at which temperature the structure begins to decompose. Thermal decomposition begins at a higher temperature (by *ca.* 100 °C) in nitrogen.

As-prepared samples of the solid, heated under vacuum to remove any residual water, display Type I isotherms for N_2 adsorption at 77 K (Fig. 5), with a maximum uptake of around 21 wt%, corresponding to an uptake of 168 cm^3(stp) g^{-1}, a pore

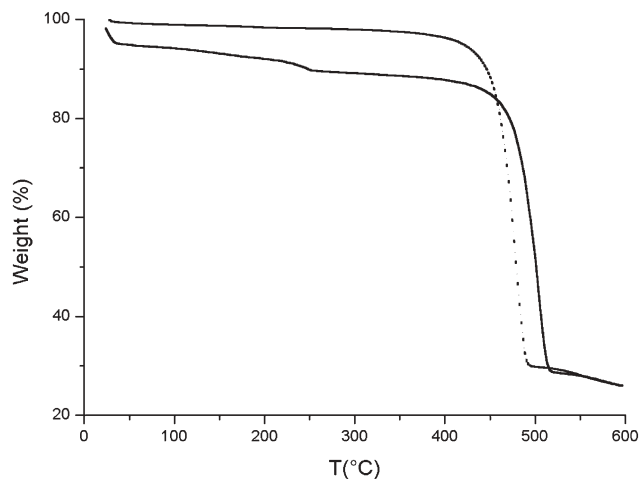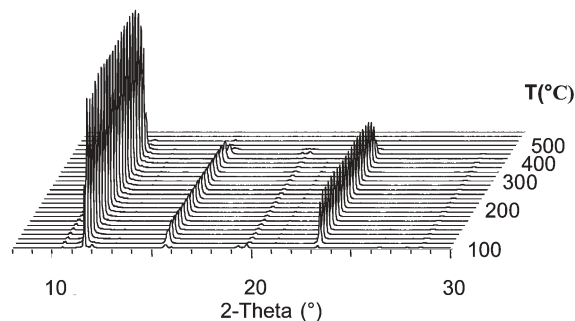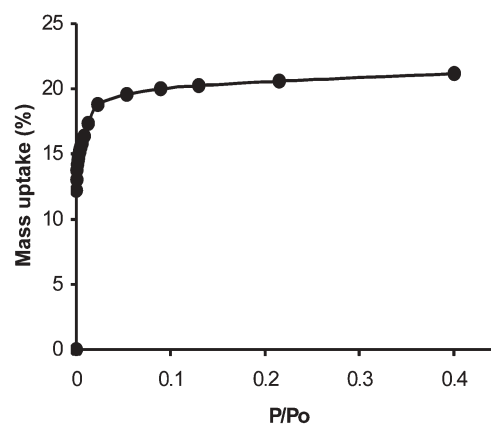volume of 0.26 cm^3 g^{-1}. This corresponds to *ca.* 32 molecules of nitrogen per unit cell of the framework, or two per channel per unit cell repeat along the x axis. The apparent discrepancy between the apparent free diameter of the channels (*ca.* 3 Å) and the ease with which the solid takes up N_2, the kinetic diameter of which is normally estimated at 3.6 Å,[3] suggests the framework may be

able to adjust to accommodate guests. Interesting behaviour of that kind has recently been described for hydrogen in an organic–inorganic hybrid.[15] In an extreme case, if the aromatic rings of one set of terephthalate linkers along the *a* axis were to rotate by 90°, they would give rise to cavities that could hold spheres *ca.* 6 Å in free diameter.

The scandium terephthalate differs strongly from other trivalent metal framework terephthalates prepared hydrothermally in a similar way. Aluminium and chromium terephthalates of the MIL-53 structure type are built up from chains of metal octahedra that are corner-sharing *via* a hydroxyl group,[10,11] whereas the chromium terephthalate based on μ_3-oxo trimers crystallises with the remarkable open framework MIL-101 structure.[16] The lack of any easily removable coordinated species in the scandium terephthalate results in higher thermal stability than for the other phases, the TGA of which indicate the onset of weight loss around 100 °C lower in temperature. Further experiments are in progress to elucidate the adsorption and structural properties of the title compound and the synthesis and crystal chemistry of other scandium carboxylates.§

Notes and references

‡ $Sc_2(O_2CC_6H_4CO_2)_3$ was prepared hydrothermally within a Teflon-lined Parr autoclave from a mixture of scandium nitrate (0.34 g $Sc(NO_3)_3 \cdot 3H_2O$, Alfa Aesar, 99%) and terephthalic acid (0.166 g, Aldrich, 98%) in *ca.* 5 ml distilled water at 220 °C for 3 days. The molar ratios of the synthesis mixture were $Sc(NO_3)_3 : HO_2CC_6H_4CO_2H : H_2O = 1.2 : 1 : 300$. The product was filtered and yellow crystals of the title phase, (0.2 × 0.2 × 0.16 mm³), were separated from unreacted terephthalic acid by suspension in ethanol, ultrasonication and decanting. Elemental Analysis: calculated: C, 49 wt%, observed: C, 46 wt%, indicating *ca.* 6 wt% water present. The phase can also be prepared using scandium oxide as the scandium source, but crystal size is smaller and the preparations are much slower due to the limited solubility of the scandium oxide.

§ Crystal data for $Sc_2(O_2CC_6H_4CO_2)_3$, M = 582.26 g·mol⁻¹, orthorhombic, space group *Fddd*, a = 8.7550(3) Å, b = 20.7786(7) Å, c = 34.4075(13) Å, V = 6259.3(4) Å³, Z = 8, D_c = 1.236 g cm⁻³, $F(000)$ = 2352, T = 293(2) K, 2.37° < θ < 40.31°, −15 < h < 15, −37 < k, 37, −62 < l < 62, $R1$ = 0.0315, $wR2$ = 0.096 for 4213 reflections with $Fo > 4\sigma (Fo)$ and 89 parameters ($R1(F^2)$ = 0.0428 (all data)), highest residual e⁻ density, 0.846; deepest hole −0.679. Intensity data from a crystal of dimensions 0.2 × 0.2 × 0.16 mm³ were obtained on a Bruker APEX X8 diffractometer using monochromated Mo K$_\alpha$ radiation (λ = 0.71073 Å). Data were corrected for Lorentz, polarisation and absorption effects. Structure solution and refinement were performed. CCDC 271099. See http://dx.doi.org/10.1039/b506677h for crystallographic data in CIF or other electronic format. The X-ray powder profile was matched using the structure parameters determined from single crystal diffraction, confirming that the sample could be prepared with high purity.

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