A porous chiral framework of coordinated 1,3,5-benzenetricarboxylate: quadruple interpenetration of the (10,3)-a network

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The chiral and porous cubic coordination polymer $Ni_3(btc)_2(py)_6(eg)_6{\cdot}x eg{\cdot}yH_2O$ (btc = 1,3,5-benzenetricarboxylate, py = pyridine, eg = ethylene glycol, $x \approx 3, y \approx 4$) is based on the interpenetration of four independent (10,3)-a networks, and contains large interconnected cavities with diameter 16 Å which may be desolvated without irreversibly destroying the porous framework structure.

The search for porous chiral solids is driven largely by a desire to perform enantioselective separations and syntheses.[1] The only two chiral zeolites known, zeolite β[2] and the titanosilicate ETS-10,[3] are both polymorphic, and samples currently retain one handedness only over a few crystallographic layers. Chiral, porous solids have very recently been resolved by the formation of single crystals: $NaZnPO_4{\cdot}H_2O$[4] consists of a tetrahedral framework containing water-filled channels, $Co(tn)_3{\cdot}Al_3P_4O_{16}{\cdot}2H_2O$[5] (GTex-2) consists of aluminophosphate layers separated by layers of the template, $Cd(tcm)[B(OMe)_4]{\cdot}x$MeOH[6] ($x \approx 1.6$) consists of sixfold helices containing methanol of solvation, and $Zn_2(btc)(NO_3){\cdot}H_2O{\cdot}5C_2H_5OH$[7] contains a single (10,3)-a network.[8] The last of these, as well as three achiral btc metallate phases,[9] shows structural stability to removal of solvent.

Here, we report the preparation of an air-stable nickel(II) salt of btc with spontaneous resolution from achiral starting materials. The material is novel in containing four interpenetrating (10,3)-a networks of the same handedness, through which lie solvent-filled pores of an unprecedented size. These pores may be desolvated completely at 115 °C to leave a poorly crystalline material with empty chiral cavities. The crystallinity of the interpenetrating lattice may be regenerated by resolvating this material with a variety of solvents.

Batches of single crystals consisting of a 50 : 50 mixture of enantiomers were synthesised by slow diffusion techniques,† and the crystal structure was determined by X-ray diffraction at 150(2) and 295(2) K.‡ $Ni_3(btc)_2(py)_6(eg)_6{\cdot}x eg{\cdot}yH_2O$ is cubic, and is the first molecular material to crystallise in the chiral space group $P4_232$. The chiral network self-assembles due to unique interactions between the ligands in the first coordination sphere of the six-coordinate Ni^{II}. The two axial positions of the octahedron are occupied by tridentate btc anions while the equatorial positions are occupied equally by eg/H_2O and py (Fig. 1). Hydrogen bonding between the non-coordinated oxygen atom of the btc carbonyl group and the equatorial alcohol/H_2O group [O(11)···O(2) 2.60 Å] produces an approximately orthogonal orientation of the *trans* btc groups bound to Ni^{II}. This hydrogen-bonded arrangement, which appears to be highly uncommon, is the structural key to the formation of the chiral framework.

In the (10,3)-a network, chirality arises from the < 100 > fourfold and < 111 > threefold helices of the same handedness propagating in all crystallographically equivalent directions. Here the 11.3 Å separation between neighbouring btc prevents interpenetration of networks of opposite chirality (such as that resulting in a racemic crystal in $[Zn(tpt)_{2/3}(SiF_6)(H_2O)_2(MeOH)]$[10]) and four networks of the same handedness interpenetrate in such a way that each is related by unit translation or twofold rotation. Pseudo-tetrahedral cavities between the networks are bounded by the four btc anions per unit cell, and are linked by wide zigzag channels running along the < 111 > directions and passing through the vertices of the tetrahedra. The cavities are centred about (0,0,0) and (1/2,1/2,1/2) (Fig. 2). Approximately 28.1% of the crystal volume is occupied by free solvent,‡ so that each pore has a volume of *ca.* 600 Å^3, and a maximum diameter of *ca.* 16 Å. With the assumed Ni coordination, each contains three eg and four H_2O molecules, as determined by elemental microanalysis. The pseudo-hexagonal < 111 > channels have radii in the range 7–10 Å. There are narrower < 100 > channels with radii in the range 5–8 Å.

With heating to 115 °C, the material undergoes a colour change from blue to green. Thermogravimetry§ and elemental microanalyses§ are consistent with the loss of six eg and one py to leave $Ni_3(btc)_2(py)_5(eg)_3(H_2O)_4$. This is accompanied by a severe broadening of the X-ray powder diffraction (XRPD) pattern.¶ Exposure to eg, EtOH and MeOH vapour at ambient conditions in all cases led to a considerable sharpening of the XRPD pattern¶ indicating a drastic increase in crystallinity with the resolvation of the lattice. This implies that the partially desolvated material, $Ni_3(btc)_2(py)_5(eg)_3(H_2O)_4$, contains large

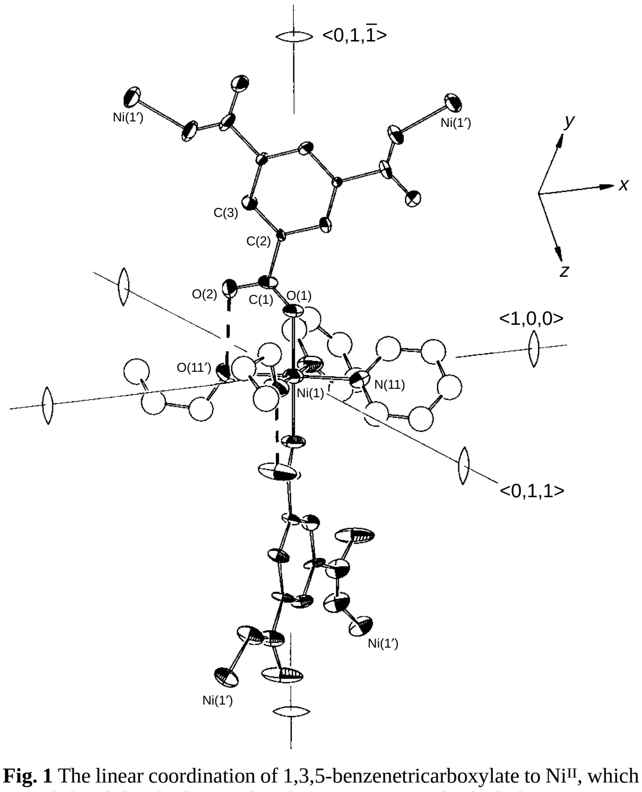

Fig. 1 The linear coordination of 1,3,5-benzenetricarboxylate to Ni^{II}, which is stabilised by hydrogen bonding to equatorial alcohol/H_2O groups (indicated by the dashed lines). The three orthogonal twofold rotation axes passing through the Ni are shown. All atoms are shown with 30% thermal ellipsoids. For clarity, only one orientation of the highly disordered fragment is shown, and hydrogen atoms have been omitted.

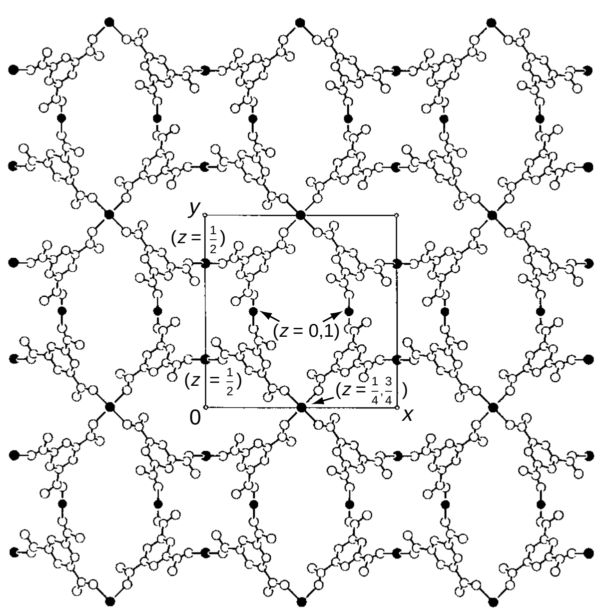

Fig. 2 Axial projection of the structure (for clarity, the equatorial ligands of the Ni^{II} cations and the solvent species occupying the pores have been removed, and only one of the two disordered orientations of the 1,3,5-benzenetricarboxylate is shown). Large, pseudo-tetrahedral solvent-filled cavities are centred about (0,0,0) and (1/2, 1/2, 1/2), and are linked by wide channels along the <111> and <100> directions. A view along (111) is presented as the graphical abstract.

empty chiral cavities, and that the relatively inflexible (10,3)-a network structure is retained throughout the cycle.

The chemical significance of the first-sphere hydrogen bonding in orienting the helix-forming btc anions is shown by the formation of isomorphous structures, either by resolvation or direct growth, with MeOH and EtOH replacing eg. The choice of ligands around the metal centre thus promises to greatly influence the chemical nature of the chiral pores in this new framework structure.

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Footnotes and References

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† Batches of large, octahedral, clear blue crystals (up to 2 × 2 × 2 mm) were grown under ambient conditions over a period of four weeks by slow diffusion of pyridine (1 mmol) into a stoichiometric 2 : 3 solution of trimesic acid (1,3,5-benzenetricarboxylic acid, 0.10 mmol) and $Ni(NO_3)_2\cdot6H_2O$ (0.15 mmol) in ethylene glycol (20 cm^3).

‡ Structural data were collected at 150(2) K on an Enraf-Nonius DIP2000 diffractometer equipped with Mo-Kα radiation, and at 293(2) K on an Enraf-Nonius CAD4 diffractometer equipped with Cu-Kα radiation. The DIP2000 data were reduced with the HKL suite of programs.[11]

Crystal data for $Ni_3(btc)_2(py)_6(eg)_6\cdot3eg\cdot4H_2O$: $C_{66}H_{98}Ni_3N_6O_{34}$, M = 1695.63, cubic, space group $P4_232$, a = 15.922(1) and 16.025(1) Å, U = 4036.4(4) and 4115.2(4) Å^3, D_c = 1.395 and 1.368 Mg m^{-3} at 150(2) and 293(2) K, respectively, Z = 2, crystal dimensions 0.40 × 0.375 × 0.35 mm, $2\theta_{max}$ = 53.46 and 149.38°. Structure solution was by a combination of geometric considerations and Fourier techniques using SHELXL-93.[12] Full-matrix least-squares refinement on F_o^2 for 1445 and 1347 unique data (30 973 and 3320 collected, R_{int} = 0.112 and 0.0363), 124 parameters and 37 restraints converged to $wR2$ = 25.99 and 20.46 (all data), conventional R = 0.0965 and 0.0697 (1070 and 908 data with $F_o > 4\sigma F_o$), with Flack parameters 0.03(11) and −0.04(15). Cavity volumes were calculated within PLATON[13] by summing voxels more than 1.2 Å away from the van der Waals surface of the framework. CCDC 182/641.

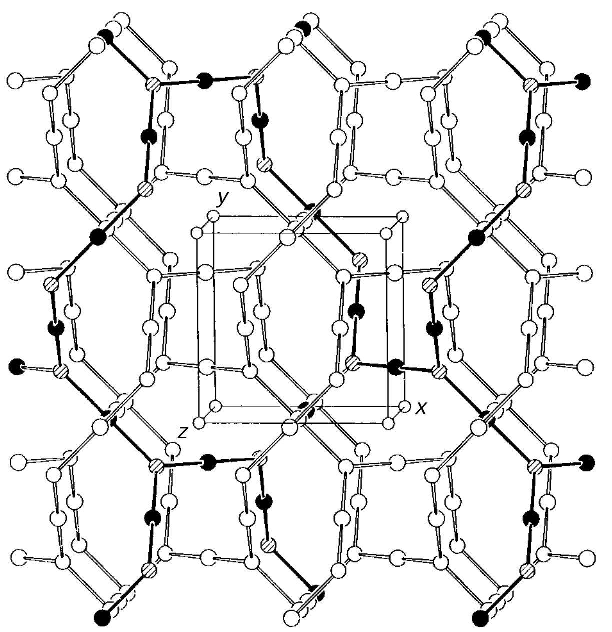

Fig. 3 Conceptual diagram showing the interpenetration of four 'clockwise' (10,3)-a networks. One of the four networks is highlighted such that the blackened circles represent Ni atoms and the hatched circles represent centres of the benzene rings.

§ In the temperature range 90–120 °C the material loses *ca.* 30% of its mass to form $Ni_3(btc)_2(py)_5(eg)_3(H_2O)_4$. In the range 120–380 °C there is a loss of a further 35%, equal to the mass of the remaining neutral species.

¶ Ground samples were sealed in 0.5 mm Lindemann capillaries and mounted on a D5000 Siemens X-ray powder diffractometer. For the [210] reflections at 2θ = 12.3°, FWHM = 0.086, 0.151, 0.165 and 0.095° for the fresh, the two 115 °C desolvated and eg resolvated samples, respectively.

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