

Zeolite-like crystal structure of an empty microporous molecular framework

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The rigidity of the coordination polymer framework of $\text{Ni}_2(4,4'\text{-bipy})_3(\text{NO}_3)_4$ is demonstrated quantitatively by determination of the structures of both ethanol-loaded and desolvated forms, showing only a small relaxation of the structure on guest loss.

The synthesis of extended molecular frameworks¹ robust to guest exchange² and linked by coordinate or hydrogen bonds has led to suggestions that such frameworks would be suitable for applications in separations and heterogeneous catalysis.³ To date, however, there has been no direct proof by structure refinement that a completely desolvated coordination polymer can retain the same open-framework geometry (as defined by quantitative analysis of diffracted intensities) once the solvent template/guest occupying the putative void space has been removed, preventing a detailed assessment of claims for zeolite-like behaviour. Previous single crystal studies are restricted to cell dimension measurement on partly desolvated systems without structure analysis.⁴ Here, we report the guest exchange chemistry and the first full crystallographic characterisation of a microporous molecular framework coordination polymer in both the solvated and completely desolvated state. Guest loss is fully reversible on a single crystal and causes no observable increase in crystal mosaicity. The refinement of data collected *in situ* on the desolvated crystal proves that the open-channel geometry is retained in the total absence of the guest, demonstrating a direct structural and chemical link with the large family of zeolite frameworks and obviating the possible problem of guest resorption on cooling present in *ex situ* studies.

Crystals of **A**, $\text{Ni}(\text{bpy})_{3/2}(\text{NO}_3)_2 \cdot \text{EtOH}$ (bpy = 4,4'-bipyridine), were grown and sealed in capillaries containing mother-liquor to prevent desolvation. Isomorphous salts containing water and CS_2 have recently been reported by other workers.^{5,6} Our structural refinement† reveals the interposition of chiral bilayers of opposite handedness to form a tongue-and-groove type structure (as represented schematically in the inset of Fig. 1). The bilayers, which take the form of the 8^210 network,⁷ result from the T-shaped coordination about nickel of three bpy units (Fig. 1). The pseudo-square-pyramidal nickel coordination is completed by two nitrate groups. Of the two crystallographically distinct bpy units, one links the nickel centres to form parallel chains in the *ab* plane and the other links neighbouring layers of chains along *z*. Although the layered array of coordinate bonds between Ni and bpy suggests two-dimensional interactions, closer inspection of the structure reveals C–H...O hydrogen bonds between the nitrate anions bound directly to the metal and the bpy groups of every second bilayer (Fig. 1). This interlayer interaction acts together with the Ni–bpy coordinate bonds within the bilayer to impart a three-dimensional character to the structure, which may be considered as the interpenetration of two semi-regular $6^4(6,10)^1$ -type 3-D networks.⁷

The interlocking of the bilayers produces channels of dimensions 6 by 3 Å parallel to *a* which are occupied in the as-grown material by ethanol. The ethanol molecule forms a single hydrogen bond to one of four neighbouring nitrate groups coordinated to nickel. These guests are liberated slowly at room temperature (50% of the ethanol is lost within 1 h at 25 °C under

dry N_2). Complete and rapid guest desorption occurs with heating to 100 °C, beyond which the empty framework material $\text{Ni}(\text{bpy})_{3/2}(\text{NO}_3)_2$ **B** is stable to 230 °C. The desolvated phase has been shown to have microporosity by N_2 sorption measurements⁵ and will take up H_2O at room temperature, with other guests including MeOH, EtOH and PrOH.

The structural consequences of desorption were studied by single crystal X-ray diffraction. The evolution of the unit cell on desorption is shown in Fig. 2, as measured *in situ* by heating a crystal at 20 K h^{-1} under dry dinitrogen. With complete desolvation of the lattice at 375 K there is a 2.4% decrease in cell volume. The robust nature of the framework is reflected in the retention of similar mosaicity of the crystal upon desolvation, allowing structural refinement of the empty co-ordination polymer framework. The refined structure and flat nature of the final difference Fourier maps demonstrate that empty channels, of dimensions 6×3 Å, are retained on desolvation (Fig. 3). Guest loss does not involve symmetry change or channel volume collapse, unlike the extended hydrogen bonded network of $[\text{Co}(\text{H}_2\text{O})_6]\text{H}_2(\text{TC-TTF}) \cdot 2\text{H}_2\text{O}$.⁸ Quantitative assessment of

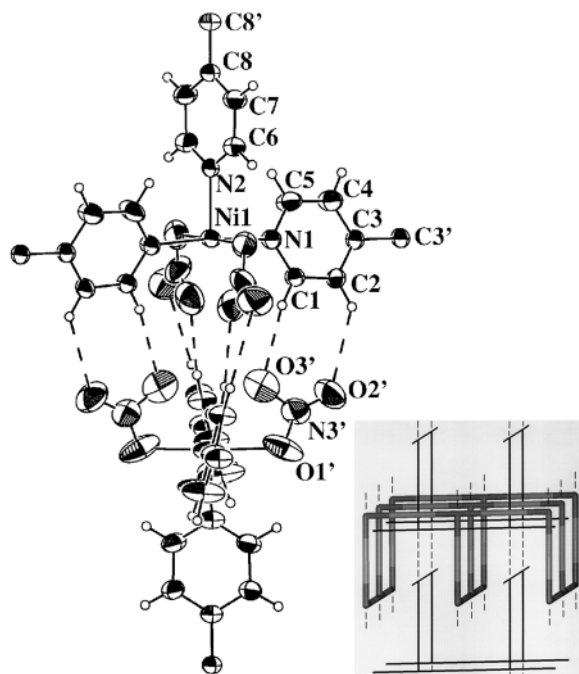


Fig. 1 The structural motif of **A** and **B**, showing labelling of all atoms in the asymmetric unit of the empty molecular framework **B** at 375 K (30% probability thermal ellipsoids). The T-shaped coordination of 4,4'-bpy about Ni gives rise to the formation of interlocking two-dimensional bilayers, as represented diagrammatically in the inset. For clarity one of the interlocking bilayers is highlighted. The chains represent linear $\text{Ni}(\text{bpy})$ strands in the *ab* plane connected into bilayers of chains at different heights along *c* by bpy groups. The torsion angle between the two sets of chains in a bilayer relaxes upon guest loss as described in the text. Multiple hydrogen bonding interactions impart a 3D nature to the framework structure ($\text{C1} \cdots \text{O3}'$ 3.536(7), $\text{H1} \cdots \text{O3}'$ 2.35, $\text{C2} \cdots \text{O2}'$ 3.412(7), $\text{H2} \cdots \text{O2}'$ 2.76 Å). Each dashed line in the inset represents eight of the C–H...O interactions in the main figure.

the channel volume⁹ reveals that it is almost unchanged: the calculated ethanol-filled volume of **A** is 808.0 Å³ per unit cell (20.6% of crystal volume) compared to a void volume of 793.8 Å³ (20.1%) in **B**. Removal of the ethanol atoms from the refined structure followed by treatment of the data with the SQUEEZE

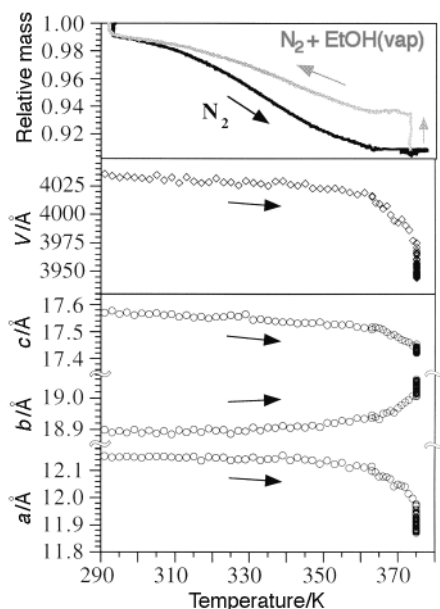


Fig. 2 Evolution of the mass, orthorhombic unit cell volume (Å³) and axial parameters (Å) during the desorption transition **A** → **B**, as measured by thermogravimetry and single crystal X-ray diffraction. The grey curve of the TGA plot is of the sorption transition **B** → **A**, performed by cooling **B** under 5 Pa partial pressure of EtOH vapour in a stream of dry N₂.

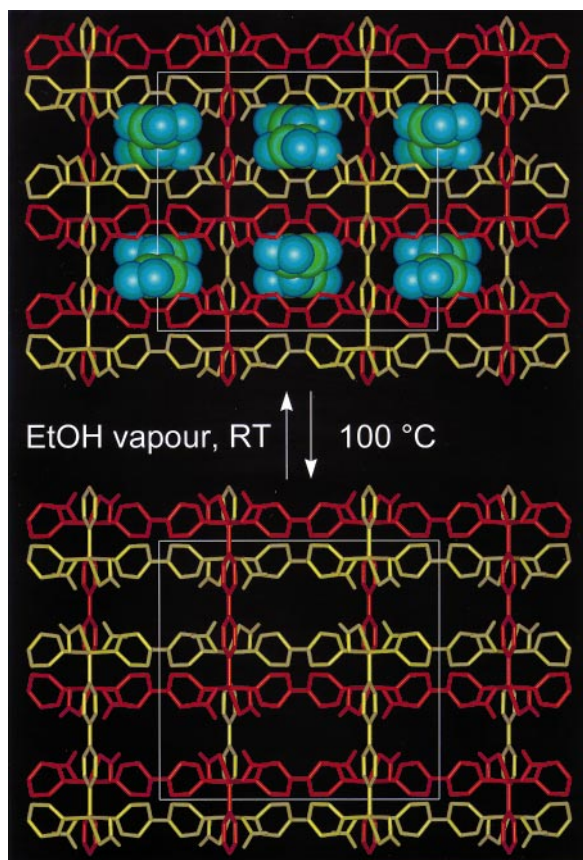


Fig. 3 Structural projections down the *a*-axis, drawn to scale, showing the complete removal of disordered ethanol molecules from **A** to form **B**. The desolvated structure, **B**, contains empty one-dimensional channels running along the *x* direction which occupy 20% of the crystal volume and have dimensions 6 × 3 Å. Adjacent bilayers are shown in yellow and red, with the C and disordered O atoms of the guest as green and blue spheres.

routine⁹ suggested a cavity electron population of 24.6 e⁻ per formula unit in **A**, agreeing well with 26 e⁻ for one ethanol molecule. Similar analysis of the data from **B** yields a cavity population of only 0.8 e⁻ per formula unit, demonstrating there is no significant ordered or disordered electron density in the channels. The average shift in framework atomic positions with desorption is 0.06 Å, and the observed Ni–bpy distances remain unchanged within error, as found for the T–O distances in hydrated and dehydrated Cu zeolite Y.¹⁰ The main structural relaxation of the framework is a subtle scissor-like action of the bilayers, leading to a decrease in the bilayer torsion angle (defined in Fig. 1) from 65.5 to 63.9°. This small distortion accompanies a 2.3% decrease in *a* and a 0.9% increase in *b*. The multitude of hydrogen bonding interactions between bilayers imparts stability to the structure in the *z* direction, as evidenced by the small decrease in *c* of 1.0%.

The present structure refinements represent the first definitive demonstration of the retention of structural integrity of a coordination polymer framework upon complete desolvation, confirming the analogy with zeolites suggested by sorption and powder diffraction measurements.

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Notes and references

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‡ *Single crystal X-ray data*: for **A**: C₁₇H₁₈N₅Ni₁O₇, *M* = 463.07, *T* = 293(2) K, orthorhombic, space group *Ccca*, blue platelet, *a* = 12.156(2), *b* = 18.891(3), *c* = 17.584(3) Å, *V* = 4038.0(12) Å³, *Z* = 8, *D_c* = 1.523 Mg m⁻³, *μ* = 1.841 mm⁻¹. Data were collected on an Enraf-Nonius CAD4 diffractometer with Cu-Kα (*λ* = 1.54180 Å) radiation. The structure was solved with SHELXS-86 and refined within SHELXL-93.¹¹ Refinement with full matrix least-squares on *F_o²* (data/restraints/parameters = 866/17/130) converged to *R*₁ = 0.0848, *wR*₂ = 0.2028 [for 413 data with *I* > 2σ(*I*)]; *R*₁ = 0.1728, *wR*₂ = 0.2435 (all data). Disorder in the nitrate and bpy ligands was modelled as described in the .cif file.

For **B**: C₁₅H₁₂N₅Ni₁O₆, *M* = 417.01, *T* = 375(2) K, orthorhombic, space group *Ccca*, blue platelet, *a* = 11.883(1), *b* = 19.049(1), *c* = 17.415(1) Å, *V* = 3942.0(5) Å³, *Z* = 8, *D_c* = 1.405 Mg m⁻³. Data were collected on an Enraf-Nonius DIP2000 diffractometer equipped with Mo-Kα (*λ* = 0.71073 Å) radiation, Eu/Ba image plate detectors and an Oxford Instruments nitrogen gas cryostream. The structure was refined with SHELXL-93¹¹ from data reduced with the HKL suite of programs.¹² Full matrix least-squares refinement on *F_o²* (data/restraints/parameters = 1957/0/124) converged to *R*₁ = 0.0676, *wR*₂ = 0.2085 [for 1480 data with *I* > 2σ(*I*)]; *R*₁ = 0.0819, *wR*₂ = 0.2210 (all data). *μ* = 1.023 mm⁻¹. CCDC 182/1136. See <http://www.rsc.org/suppdata/cc/1999/375/> for crystallographic files in .cif format.

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