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Nanoporosity of an interpenetrated NbO-type molecular framework studied by single crystal X-ray diffraction†

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The molecular framework $[\mathrm{Fe(NCS)_2(tmbpz)_2}]$ (tmbpz = 3,3′,5,5′-tetramethyl-4,4′-bipyrazolyl) consists of a robust doubly interpenetrated NbO-type network that remains stable on the removal of solvent guest molecules.

Molecular framework materials have a variety of possible compositions and topologies, and may exhibit interesting host–guest and/or electronic functional properties. Novel combinations of properties can be envisaged for 'functionalised' frameworks that do not collapse irreversibly on removal of the solvent of crystallisation. Consequently, there is general interest in robust frameworks that display sufficient structural integrity for the empty host to be characterised by X-ray diffraction analysis.[1,2] These frameworks are characteristically held together in three dimensions by strong interactions—coordination bonding, hydrogen bonding, π-stacking interactions, or polycatenation.

As part of our ongoing investigations into the incorporation of spin crossover centres into nanoporous molecular frameworks,[2] the multiply coordinating ligand 3,3′,5,5′-tetramethyl-4,4′-bipyrazolyl (tmbpz) was chosen for the synthesis of frameworks containing *trans*-dithiocyanatotetrapyrazolyl iron(II) centres. The unusual skew coordination geometry of the ligand and its capacity to form multiple hydrogen bonds result in strong and unusually directed stabilising interactions.[3,4] In combination with iron(II), the ligand was expected to form robust 3-D molecular frameworks of diverse architectures.

The ligand was synthesised as described in the literature.[4] Crystals of $[\mathrm{Fe(NCS)_2(tmbpz)_2}]\cdot\frac{2}{3}\mathrm{MeCN}$ (**A**·⅔MeCN; MeCN = acetonitrile) were grown as hexagonal rods by slow diffusion of iron(II), thiocyanate and tmbpz in MeCN. Structural refinement‡ indicates that the iron centres are coordinated in distorted octahedral fashion by two *trans* thiocyanato ligands and four tmbpz ligands. The resulting structure consists of two equivalent interpenetrated NbO-type nets related by a [001] translation, the basic structural unit of which is a 3-D right-angled hexagon (Fig. 1). The interpenetration is stabilised by a network of hydrogen bonds between them, each sulfur atom forming two hydrogen bonds to different pyrazole N–H groups (Fig. 1). The framework houses 1-D solvent-filled channels running parallel to the *c* axis, each consisting of small cavities (diameter 5.5 Å) connected by hexagonal windows (3.5 Å) of sulfur atoms. In the as-grown material the pores each contain one MeCN molecule disordered about the 3-fold axis and oriented such that its bonding axis is aligned approximately along the channel axis (Fig. 2).

The formation of NbO-type ((6,4)-net) rather than square grid ((4,4)-net) molecular frameworks from square planar 4-connectors is rare.[5–7] The unusual architecture of **A**·⅔MeCN can be attributed primarily to steric interactions between the Me substituents on the tmbpz ligands. The 5 and 5′ Me groups extend into the second coordination sphere of the iron, forcing the four coordinating pyrazole rings into their observed orientations.[8] In addition, tmbpz has a 54.6(6)° torsion angle around its central C–C bond, also caused by interactions between the Me substituents, resulting in the relative rotation of adjacent iron coordination spheres. A similar structural feature has been used to generate NbO-type frameworks with substituted terephthalates.[6]

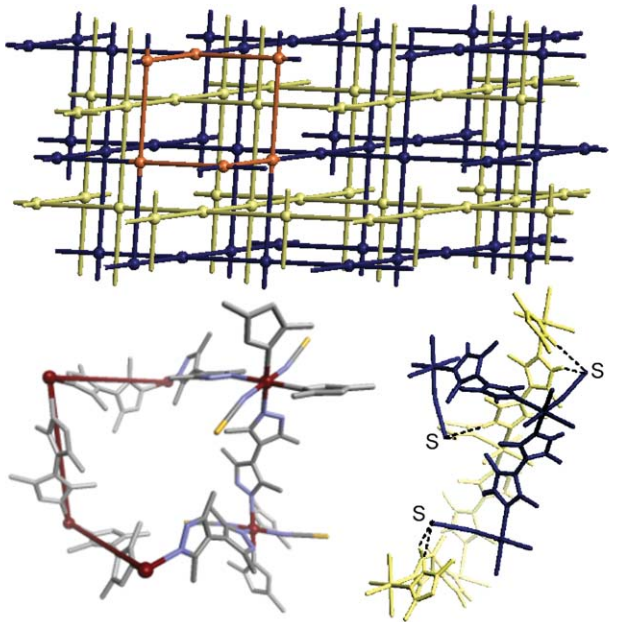

Fig. 1 (above) Schematic of interpenetrated NbO-type nets in **A**, with the structural unit, a 3-D hexagon, highlighted; (below left) the hexagon formed by tmbpz and iron(II) in **A**, with hydrogen atoms omitted for clarity; (below right) hydrogen bonds from sulfur (blue net) to pyrazole hydrogen (yellow net), methyl hydrogen atoms omitted.

We note that the interpenetration of two NbO-type nets observed here is perhaps unusual given current 'self-dual' models of lattice interpenetration;[6] however, its occurrence has been foreseen[9] and other examples exist.[7] Interpenetration appears to be favoured in the present case because of the stabilising hydrogen bonds that form as a result.

The interweaving of two 3-D nets gives a host framework with multiple strong inter- and intra-framework self-interactions in three dimensions. In contrast, host–guest interactions appear to contribute comparatively little to the overall stability of **A**·⅔MeCN, there being no short hydrogen bonding interactions between the MeCN guests and the framework host.

Thermogravimetry of **A**·⅔MeCN under dry dinitrogen gas indicates that complete desorption of MeCN (5% observed mass decrease) occurs by 80 °C, and the desolvated phase **A** is stable to 200 °C. Complete sorption of MeCN occurs on cooling under MeCN vapour.† To determine the structural consequences of MeCN desorption a single crystal of **A**·⅔MeCN was heated in an open capillary at 400 K for 48 h to form **A**, the capillary sealed, and a single crystal X-ray data collection performed at 150 K.‡ Integration of the pore electron density[10] gave 0.7 e^- per formula unit for **A**, consistent with complete MeCN desorption, compared to 14 e^- per formula unit for **A**·⅔MeCN (*cf.* 15.3 e^- expected).

Close comparison of the 150 K crystal structures of the parent

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† Electronic supplementary information (ESI) available: thermogravimetric data; unit cell data collected on heating; atomic shift calculations. See http://www.rsc.org/suppdata/cc/b4/b409543j/

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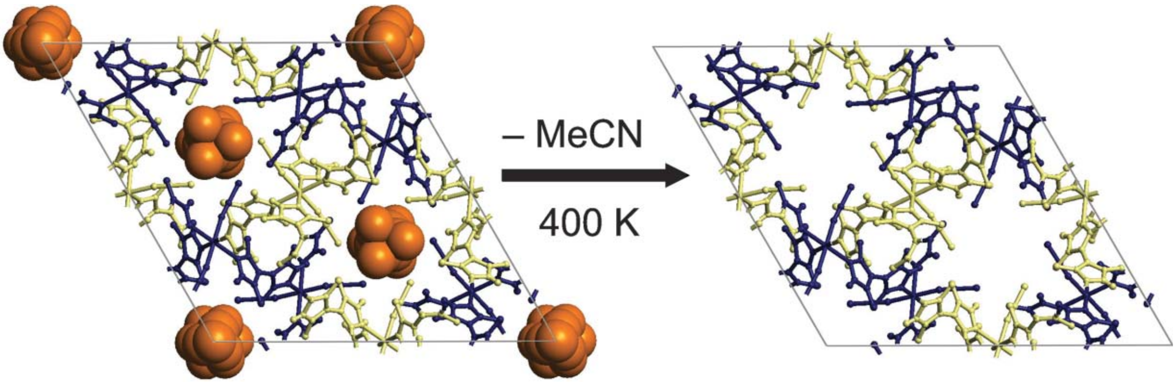

Fig. 2 Unit cells of **A**·⅔MeCN (*a* horizontal, *c* into page, interpenetrated NbO-type nets in blue and yellow, disordered MeCN in orange) and **A** (obtained by heating at 400 K for 48 h; orientation and colouring as for the solvated phase).

and desorbed phases, **A**·⅔MeCN and **A**, indicates an absence of marked structural change on MeCN desorption (Fig. 2). The calculated volume of the channels[10] is almost identical, increasing slightly from **A**·⅔MeCN (824.4 Å^3 per unit cell, or 13.6% of crystal volume) to **A** (832.5 Å^3, 13.7%). Of the unit cell parameters, *a* remains unchanged within error from **A**·⅔MeCN to **A**, while *c* decreases by 0.016(11) Å (0.15%). The maximum structural distortion occurs at the thiocyanate sulfur atom, it being shifted by 0.035 Å (displacement/esd = 17)† with a subtle rotation of the thiocyanate ligand into the pore. There is no significant shift for any non-sulfur atom (average atomic displacement/esd = 1.5). These changes are significantly smaller than those seen in other desorbed molecular framework hosts,[1,2] highlighting the unusually robust nature of this material.

The close similarity of the parent and desorbed structures is noteworthy given that the pore windows (diameter 3.5 Å) are similar in size to the MeCN methyl group. As such, the diffusion of MeCN through the framework is expected to involve local structural deformation, a feature that is consistent with previous observations that molecular frameworks may accommodate localised deformations without losing overall integrity.[11] To determine whether any bulk structural relaxation occurs during the desorption process, a single crystal of **A**·⅔MeCN was heated under dry dinitrogen *in situ* on the X-ray diffractometer from 280 to 375 K at 20 K h^{-1}. Unit cell parameters obtained during heating showed variations attributable to thermal expansion.† At 375 K, collection and refinement of three full crystallographic data sets demonstrated that the MeCN occupancy fell from 60% to 41% over a period of 24 h.† The crystal was then cooled to 150 K and a further structure (**A**·0.27MeCN)‡ determined at this temperature. This structure was refined as for **A**·⅔MeCN, except that the thermal parameters of the MeCN atoms were fixed at appropriate values based on values obtained from **A**·⅔MeCN, and the solvent occupancy was allowed to refine. No evidence was found for the ordering of guest vacancies, which could take the form of symmetry lowering, satellite reflections or rods/planes of diffuse scattering. This suggests any guest–guest or framework-mediated communication of guest location is insufficient to prevent the entropically favoured random distribution of the MeCN guests.

In summary, **A** is one of the very few molecular framework materials known to support void volume without structural collapse. The single crystal diffraction data presented here show that no significant structural relaxation occurs on guest desorption, and that the void channels remain intact on partial and complete removal of the MeCN guest. This remarkable stability can be attributed to the strength of the interactions holding the 3-D framework in place: each NbO-type net is connected by coordination bonding in three dimensions, and slippage of the nets relative to each other is prevented by an extensive hydrogen bonding network.

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Notes and references

‡ Single crystal X-ray data: for **A**·⅔MeCN: $C_{22}H_{28}FeN_{10}S_2\cdot\frac{2}{3}(C_2H_3N)$, $M = 579.88$, hexagonal, $a = 25.283(17)$, $c = 10.962(11)$ Å, $V = 6068(8)$ Å^3, $T = 150(2)$ K, space group $R\bar{3}$ (no. 148), $Z = 9$, μ(Mo–Kα) = 0.749 mm^{-1}, data/restraints/parameters 3193/0/171 ($R_{\text{int}} = 0.0771$), $R1 = 0.0575$, $wR2 = 0.1324$ ($I > 2\sigma(I)$); for **A**: $C_{22}H_{28}FeN_{10}S_2$, $M = 522.51$, hexagonal, $a = 25.2831(14)$, $c = 10.9463(13)$ Å, $V = 6059.8(9)$ Å^3, $T = 150(2)$ K, space group $R\bar{3}$, $Z = 9$, μ(Mo–Kα) = 0.746 mm^{-1}, data/restraints/parameters 3237/0/160 ($R_{\text{int}} = 0.0412$), $R1 = 0.0421$, $wR2 = 0.0851$ ($I > 2\sigma(I)$); for **A**·0.27MeCN: $C_{22}H_{28}FeN_{10}S_2\cdot 0.27(C_2H_3N)$, $M = 563.80$, hexagonal, $a = 25.3021(14)$, $c = 10.9672(13)$ Å, $V = 6080.5(9)$ Å^3, $T = 150(2)$ K, space group $R\bar{3}$, $Z = 9$, μ(Mo–Kα) = 0.745 mm^{-1}, data/restraints/parameters 3107/0/168 ($R_{\text{int}} = 0.0422$), $R1 = 0.0369$, $wR2 = 0.0714$ ($I > 2\sigma(I)$). CCDC 243653–243658. See http://www.rsc.org/suppdata/cc/b4/b409543j/ for crystallographic data in .cif or other electronic format.

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