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Iron(II) Molecular Framework Materials with 4,4'-Azopyridine

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Three new iron(II) molecular-framework materials incorporating the bridging ligand 4,4'-azopyridine (azpy) have been synthesized and structurally characterized: $Fe_2(azpy)_4(NCS)_4 \cdot (azpy)$ (A), $Fe(azpy)(NCSe)_2(EtOH)_2 \cdot (azpy)$ (B), and $Fe(azpy)_2(NCSe)_2 \cdot 2(MeCN)$ (C). A and C consist of non-interpenetrating (4,4) grids of iron(II) centres bridged by azpy ligands with non-coordinating azpy ligands or acetonitrile molecules occupying the spaces within and between the layers. For B, hydrogen-bonding interactions between coordinated ethanol molecules and noncoordinated azpy ligands link linear Fe–azpy chains to give a two-dimensional framework.

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Interest in molecular-framework materials constructed from metal ions and organic bridging ligands continues to broaden as their diverse properties and subsequent potential applications continue to be realized.^[1,2] Already there are many examples of these materials that have been designed with specific structures and interesting properties such as porosity,^[3–6] chirality,^[7] and magnetism.^[8,9]

With an interest in combining spin switching with nanoporosity we have recently focussed synthetic efforts on the incorporation of spin crossover centres into open molecular frameworks.^[10,11] The first such material, $[Fe_2(azpy)_4-(NCS)_4] \cdot (guest)$ (\mathbf{D}_{guest}),^[10] consists of interpenetrating two-dimensional grids of Fe(II) centres linked by azpy ligands (Scheme 1). The coexistence of both nanoporosity and spin crossover Fe(II) centres in \mathbf{D}_{guest} has resulted in a material where the spin transition is 'triggered' by sorption of a guest alcohol molecule. Here, further investigations of Fe(II) framework materials with the azpy ligand have been undertaken, including attempted preparations of selenocyanate analogues of \mathbf{D}_{guest} , with the expectation that the resulting increased crystal-field splitting may yield materials with higher spin crossover temperatures.^[12]

 $[Fe_2(azpy)_4(NCS)_4] \cdot (azpy)$ (**A**) was isolated as a minor product from the preparation of **D**_{1-PrOH} as brown platelet crystals. Subsequent attempts to intentionally synthesize **A** with appropriately modified stoichiometry were unsuccessful, with repeated syntheses exclusively producing **D**_{1-PrOH}. The structure of **A** was solved and refined in the monoclinic space group *C*2/*m*. The refinement revealed rhombic (4,4)



Scheme 1. Structure of 4,4'-azopyridine (azpy).

grids constructed from Fe(II) centres linked by four equatorially coordinated azpy ligands, with axial thiocyanate ligands completing the octahedral coordination sphere. Unlike in $\mathbf{D}_{\text{guest}}$, these grids do not interpenetrate but stack upon one another parallel to the (103) plane, with an interlayer separation of 4.48 Å (Fig. 1*a*). The asymmetric unit contains two Fe(II) centres located on special positions, each with one thiocyanate, one 1/2 azpy and one 1/4 azpy, defining crystallographically distinct alternate rhombic grids. The Fe1 and Fe2 octahedra are both compressed toward the thiocyanate ligands and their corresponding bond lengths are characteristic of high-spin Fe(II) and agree to within two standard deviations (Fe1-N(1/2 azpy) 2.267(6) Å, Fe2-N(1/2 azpy) 2.252(6) Å,Fe1-N(1/4 azpy) 2.204(7) Å, Fe2-N(1/4 azpy) 2.207(7) Å, Fe1-N(CS) 2.069(7) Å, Fe2-N(CS) 2.081(8) Å). The majority of the angles about the octahedra are ideal (90°) , with only a slight distortion in the angle between the thiocyanate and the 1/2 azpy (87.1(2) and 89.4(3)° for Fe1 and Fe2, respectively). Both 1/4 azpy ligands of the asymmetric unit define two-fold disordered azo bonds, where the four nitrogen positions are defined by a single atom (N4 or N14). Non-coordinated azpy ligands occupy linear channels along the crystallographic *c*-axis. The atom positions of the guest azpy molecule were clearly identified from the difference map but required several restraints for stable refinement. No significant framework-guest interactions were evident in the structure. Without sufficient product, the potentially interesting magnetic and guest-exchange properties of A could not be explored.

The first attempt to synthesize selenocyanate analogues involved mimicking the preparation of \mathbf{D}_{EtOH} and substituting ammonium thiocyanate with potassium selenocyanate. These diffusions yielded orange crystals that have been structurally characterized as [Fe(azpy)(NCSe)₂-(EtOH)₂] \cdot (azpy) (**B**), revealing a structural motif very

similar to that reported for the material [Fe(azpy)(NCS)2- $(MeOH)_2$ · (azpy).^[13,14] A similar supramolecular pattern has also been observed in several 4,4'-bipyridine-containing coordination frameworks.^[15–18] For **B**, linear chains of Fe(II) centres are linked by azpy ligands, with pairs of trans-coordinated selenocyanate anions and oxygen bound ethanol molecules completing the octahedral coordination sphere. All non-hydrogen atoms were modelled anisotropically and no disorder was observed in the structural refinement. The Fe(II) octahedra are elongated toward the azpy ligands (Fe-N(azpy) 2.462(19) Å, Fe-N(CSe) 2.117(2) Å, Fe-O(EtOH) 2.1148(17) Å), and are mildly distorted with N/O-Fe-N/O angles ranging from 86.91(7) to 93.09(7)°. Hydrogen-bonding interactions between the coordinated ethanol molecules and unbound azpy ligands (O12 ··· N3 2.698 Å) link parallel chains to form a pseudo twodimensional grid structure (Fig. 1b). These grids stack parallel to one another in the (101) direction. The coordination of ethanol deems the material to be of insufficient interest for both magnetic and guest-exchange studies.

Attempts to synthesize selenocyanate analogues of \mathbf{D}_{guest} were also carried out with several other solvents (methanol, acetone, acetonitrile, 1-propanol); however, only diffusions with acetonitrile were successful in producing single crystals. These brown platelet crystals differed greatly in morphology from the dark-blue rod-shaped crystals observed for \mathbf{D}_{guest} and were structurally characterized by X-ray diffraction

to be $Fe(azpy)_2(NCSe)_2 \cdot 2(MeCN)$ (C). The structure was solved and refined in the monoclinic space group C2/m. The structure consists of rhombic (4,4) grids of Fe(II) centres linked by the equatorial coordination of four azpy ligands, with two axial selenocyanate ligands completing the compressed octahedral coordination sphere (Fe1-N11(NCS) 2.115(2) Å, Fe1-N1(azpy) 2.212(7) Å, Fe1-N3(azpy) 2.237(7) Å; N-Fe(II)-N angles range from 86.1(4) to 93.79(8)°). The structurally equivalent two-dimensional grids stack in a similar fashion to that observed for A (Fig. 1c), with acetonitrile guest molecules zig-zagging through the layers (Fig. 1d). Subsequent layers are spaced 4.42 Å apart, slightly closer than the 4.48 Å spacing observed for A. The acetonitrile guest molecules exhibit two-fold symmetry related disorder. A head-to-tail hydrogen-bonding interaction was located between neighbouring acetonitrile molecules (C21 ··· N21' 3.445(9) Å). Calculations of the channel volume and composition within *PLATON*^[19] suggest a solvent-accessible volume of 29.7% and an electron population of 19 electrons per cavity, in good agreement with the expected value of 22 electrons per acetonitrile molecule.

Variable temperature magnetic susceptibility measurements were employed to investigate the spin state of **C**. The magnetic moment remained approximately constant at 5.4 μ_B on cooling from 225 to 15 K. These values are consistent with the presence of only high-spin Fe(II) sites (S = 2), with no indication of a spin-transition.



Fig. 1. Stick representations of the three crystal structures. (*a*) Stacking of four layers in A and the uncoordinated azpy ligands, the latter shown in a lighter shade. (*b*) Two-dimensional coordination and hydrogen-bonded layer in the structure of B (hydrogen bonds are shown as dashed lines). (*c*) Stacking of the layers in C with subsequent layers coloured differently. (*d*) Linear channels in C occupied by acetonitrile guest molecules (space filling representation). All hydrogen atoms, except those of the ethanol OH in B, have been omitted for clarity.

Despite a similar iron(II) coordination geometry to that present in D_{guest}, no spin crossover was observed for C. Geometric structural parameters that may influence the occurrence of spin crossover include the average iron(II)-nitrogen bond length ($d_{\text{Fe}-N}$), the global octahedral distortion (Σ : the sum of the deviation of each of the 12 cis angles) and the torsion angle of the pyridyl groups with respect to the equatorial plane of the octahedral coordination sphere (ψ) .^[20] Short $d_{\rm Fe-N}$ distances, minimal Σ and ψ angles approaching 45° (allowing maximum π back-bonding) strengthen the crystal field and stabilize the low-spin configuration. These structural parameters for C, the high-spin structure of $\mathbf{D}_{EtOH}^{[10]}$ and the desolvated material $\mathbf{D}^{[10]}$ are included in Table 1. There is no strong relationship between these parameters and the existence of spin crossover; however, those of the spin crossover Fe2 centre of \mathbf{D}_{EtOH} are collectively more favourable. For C, the parameters more closely resemble those of the spin crossover inactive Fe1 centre of D_{EtOH} . In a recent study of an extensive series of discrete $[FeL_n(NCS)_2]$ (L = N-donor ligand, n = 2 (bidentate) or 4 (unidentate)) complexes, a similar range of inter- and intra-molecular structural properties were tabulated and compared to spin crossover features.^[21] Again, no single structural reason was found to explain why spin crossover occurs in some complexes and not others, highlighting the subtle nature of the phenomenon.

Table 1. Selected structural parameters for the high-spin structures of C, D_{EtOH} ,^[10] and the desolvated material D. ^[10] Of the two crystallographically distinct iron(II) sites in D_{EtOH} only the Fe2 site exhibits spin crossover

Structure	SCO	d _{Fe-N} [Å]	Σ [°]	ψ[°]
С	No	2.188	16	60
D _{EtOH} (Fe1)	No	2.170	21	56
D _{EtOH} (Fe2)	Yes	2.167	10	52
D	No	2.252	26	47

Three new molecular-framework materials incorporating iron(II) and azpy have been synthesized and structurally characterized; **A** and **C** consist of non-interpenetrating (4,4) grids of iron(II) centres bridged by azpy ligands, while in **B**, hydrogen-bonding interactions between bound ethanol molecules and unbound azpy link linear Fe–azpy chains to give an overall two-dimensional structure. These results highlight the sensitivity of the self-assembly process that the synthesis of systems of this type rely on, with subtle changes in the chemical reagents or diffusion conditions resulting in an array of different structures. However, the synthesis of new and different examples of framework materials continues to clarify our understanding of the range and relative importance of the interactions between metals, ligands, and solvents.

Experimental

Ligand Synthesis

The synthesis of azpy was adapted from published methods.^[22,23] An aqueous solution (200 mL) of 4-aminopyridine (16.9 g, 92 mmol) was added over 40 min to an aqueous sodium hypochlorite solution (12.5% w/v, 1200 mL) at 0°C. The reaction was stirred at 0°C for a further 20 min. The orange product was extracted with diethyl ether (1500 mL) and evaporated to dryness on a rotary evaporator. The crude product was recrystallized from boiling H₂O (200 mL). Yield 10.7 g (64%). $\delta_{\rm H}$ (200 MHz, CDCl₃, TMS): 8.87 (d, 4H, ²J 6), 7.75 (d, 4H, ²J 6).

Framework Syntheses

A: A diffusion of azpy (90 mg, 0.50 mmol) and a mixture of iron(Π) perchlorate (42 mg, 0.17 mmol) and ammonium thiocyanate (25 mg, 0.33 mmol) in 1-propanol gave brown platelet crystals of **A** as a minor product (major product: **D**_{1-PrOH}). Yield approx. 20 mg (19%).

B: Diffusions of azpy (40 mg, 0.22 mmol) and a mixture of iron(II) perchlorate (28 mg, 0.11 mmol) and potassium selenocyanate (31 mg, 0.22 mmol) in ethanol gave dark yellow crystals of **B**. Yield approx. 55 mg (70%).

C: Diffusions of azpy (40 mg, 0.22 mmol) and a mixture of iron(II) perchlorate (28 mg, 0.11 mmol) and potassium selenocyanate (31 mg,

Table 2.	Crystallographic	data for A, B, and	C
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Parameter	Α	В	С
Formula	$Fe_2(C_{10}N_4H_8)_4(NCS)_4 \cdot (C_{10}N_4H_8)$	$Fe(C_{10}N_4H_8)(NCSe)_2(C_2H_6O)_2 \cdot (C_{10}N_4H_8)$	$Fe(C_{10}N_4H_8)_2(NCSe)_2 \cdot 2(CH_3CN)$
$M[g mol^{-1}]$	1265.04	726.35	716.33
T [K]	150(2)	150(2)	150(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C</i> 2/ <i>m</i> (no. 12)	$P2_1/c$ (no. 14)	<i>C</i> 2/ <i>m</i> (no. 12)
a [Å]	22.514(5)	7.2556(19)	9.2518(16)
<i>b</i> [Å]	13.402(3)	17.061(4)	20.446(4)
c [Å]	10.922(2)	12.298(3)	8.5790(15)
β[°]	101.613(4)	96.843(4)	103.215(3)
$V[Å^3]$	3228.0(12)	1511.5(7)	1579.9(5)
Ζ	2	2	2
$\rho_{\rm calc} [{\rm Mg} {\rm m}^{-3}]$	1.301	1.596	1.506
$\mu [{\rm mm}^{-1}]$	0.633	2.949	2.818
Data	4002	3573	1940
Restraints	54	0	0
Parameters	231	191	108
$R(F) \{I > 2\sigma I\}$	0.0798	0.0344	0.0344
$R(F)$ {all data}	0.1535	0.0426	0.0435
$R_{\rm w}(F^2) \{I > 2\sigma I\}$	0.2225	0.0857	0.0775
$R_{\rm w}(F^2)$ {all data}	0.3119	0.0915	0.0847
GoF	1.051	1.098	1.092

0.22 mmol) in acetonitrile gave a small number of orange platelet crystals of **C**. Yield approx. 12 mg (15%).

Structure Determinations

Diffraction data were collected on a Bruker Smart 1000 CCD equipped with $Mo_{K\alpha}$ (λ 0.71073 Å) radiation and nitrogen (100–375 K) and helium (25–375 K) cryostreams (Oxford Instruments). Crystals were mounted on a mohair fibre in a thin film of perfluoropolyether oil and quench cooled to 150 K. Full spheres of data were collected over a range of incident angles, up to 2000 frames, with a 30 s exposure time per frame. Empirical absorption corrections were applied to all data using *SADABS*.^[24] The structures were solved and refined with *SHELXTL*^[25] from data reduced with *SAINT* + ver. 6.02.^[26] Summaries of crystallographic data are given in Table 2 and full crystallographic information files are provided in the Accessory Materials.

Magnetic Susceptibility Measurements

Magnetic susceptibility data were collected using a Quantum Design MPMS 5 SQUID instrument at the School of Chemistry, Monash University. Measurements were made on uniform crystalline samples in the temperature range 15 to 225 K and at a field of 10 000 Oe.

Accessory Materials

Full crystallographic tables and magnetic data for C are available from the author or, until May 2010, the *Australian Journal of Chemistry*. Depositions are available from the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk; A: 256870, B: 256871, C: 256872).

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