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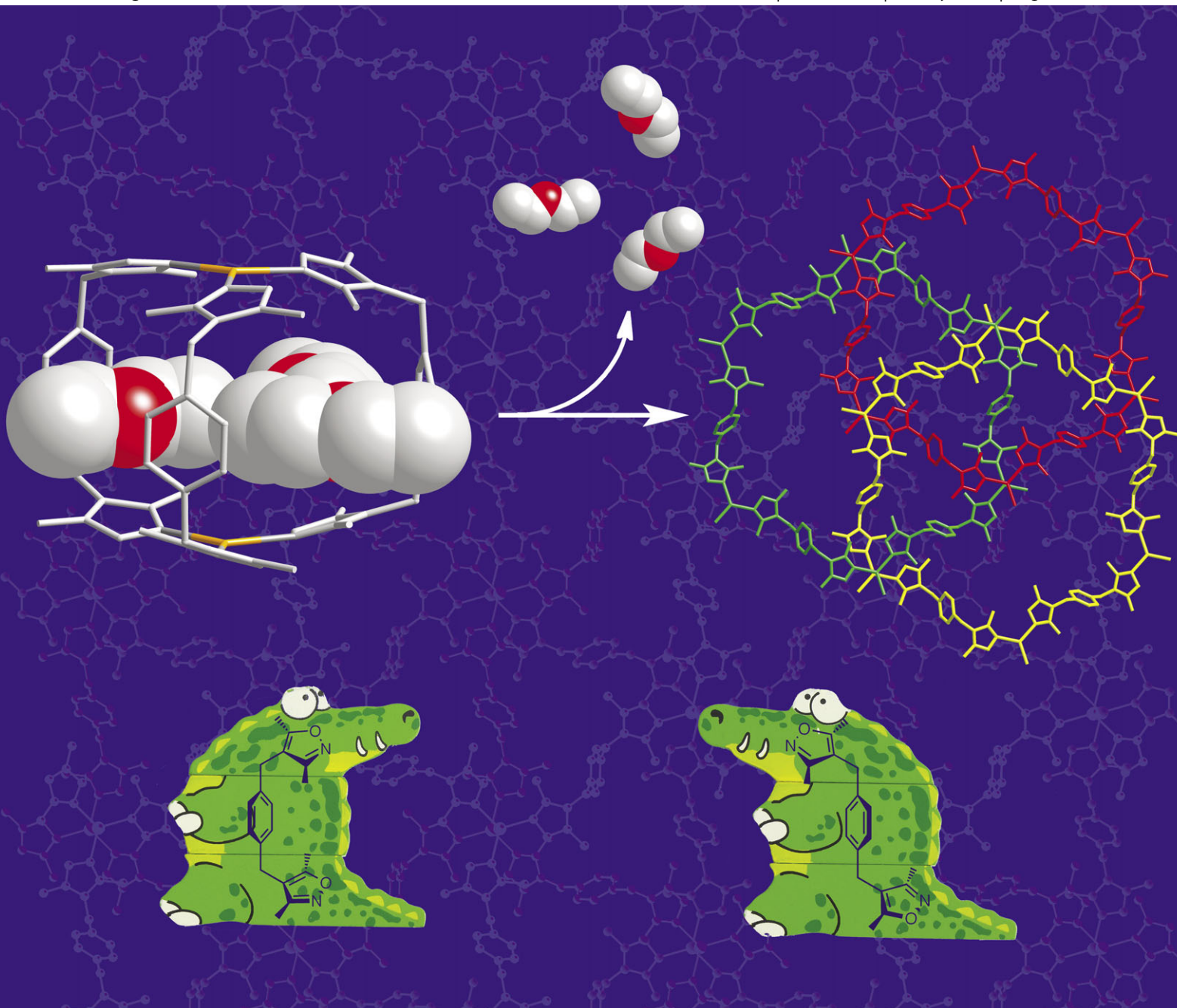
COMMUNICATION
Andrew D. Burrows *et al*.
Solid state interconversion of cages and coordination networks *via* conformational change of a semi-rigid ligand

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Solid state interconversion of cages and coordination networks *via* conformational change of a semi-rigid ligand†

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The reaction of silver(I) perchlorate with the semi-rigid ligand 1,4-bis((3,5-dimethylisoxazol-4-yl)methyl)benzene (bisox) in methanol gives a triply-interpenetrated sheet structure, but a structure containing both interpenetrated sheets and $Ag_2(bisox)_3$ cages is formed on recrystallisation from acetonitrile–diethyl ether. Rearrangement of the cages into sheets occurs on heating under vacuum, a process which involves a solid state change in conformation of the bisox ligands.

While bridging ligands are often used to generate rigid metal–organic frameworks,[1] introducing flexibility into a coordination network can allow it to reversibly respond to the presence or absence of a guest.[2] Metal–organic frameworks capable of 'breathing' are normally formed by employing metal centres that are amenable to distortions in the coordination sphere, but an alternative strategy is to incorporate the potential for flexibility into a bridging ligand. If the ligand conformations are totally unrestricted, it might be expected to adjust its conformation in a network to produce a non-porous structure. In contrast, the use of semi-rigid ligands,[3] with inherent but limited flexibility, represents an attractive strategy to form flexible frameworks.

In this communication, we report our initial studies into the silver(I) networks formed by the semi-rigid bis(isoxazolyl) ligand 1,4-bis((3,5-dimethylisoxazol-4-yl)methyl)benzene (bisox) on reaction with silver(I) perchlorate.
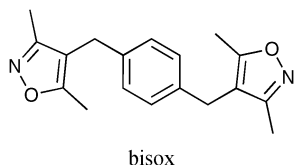
bisox

The methylene spacers between the isoxazole rings and the central benzene ring in the bisox ligand allow it to adopt several conformations. Of these, molecular mechanics suggests that the lowest energy conformation is of C_i symmetry, with the nitrogen donor atoms oriented away from each other. This is also the conformation adopted in the crystal structure of

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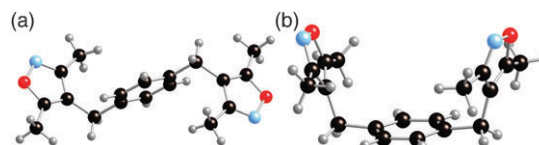[b] School of Chemistry, University of Wollongong, Wollongong, NSW 2522, Australia

Fig. 1 (a) The S- and (b) C-conformations for bisox.

bisox (see ESI†), and for ease of visualisation, we denote this the S-conformation (Fig. 1a). A rotation of 180° about one of the benzene-methylene C–C bonds generates a conformation of C_h symmetry, which we denote the C-conformation (Fig. 1b).

The reaction between bisox and silver(I) perchlorate in methanol gave crystals of $[Ag_2(bisox)_3](ClO_4)_2$ **1** suitable for a single crystal X-ray analysis.‡ The asymmetric unit of **1** contains a third of a silver(I) centre, located on a three-fold rotation axis, half of a bisox ligand, proximate to an inversion centre, and a perchlorate anion fragment, in which the chlorine and one oxygen atom are located on the three-fold rotation axis. Each silver(I) centre is trigonal planar and coordinated to three bisox ligands, which all adopt S-conformations, and link the silver centres into (6, 3) sheets.

The hexagonal 'pores' within these sheets have internal widths of 16.8 Å, and unsurprisingly interpenetration occurs to reduce the void space. Overall, the structure is triply parallel interpenetrated as shown in Fig. 2a. The layers contain Borromean links,[4] which involve three interlocked rings. The interpenetration generates triangular pores, and the perchlorate anions reside towards the top and bottom of these, between the layers, as shown in Fig. 2b. These anions form C–H⋯O hydrogen bonds with both methyl and aromatic CH groups.

The structure of **1** is related to those reported previously for the 1,4-bis(2-methylimidazol-1-ylmethyl)benzene (bismim) networks $[Ag_2(bismim)_3](BF_4)_2$ and $[Ag_2(bismim)_3](CF_3SO_3)_2$.[5] Subtle differences were seen in the two silver–bismim networks, with a change of orientation of the methylimidazolyl rings allowing accommodation of the larger triflate anion at the expense of Ag⋯Ag interactions. The bisox ligand in **1** has methyl groups on both sides of the five-membered ring, and lies approximately parallel to the silver coordination plane. The intra-sheet Ag⋯Ag distance is 2.9990(7) Å, consistent with a $d^{10}⋯d^{10}$ interaction, whereas the inter-sheet Ag⋯Ag distance is 4.306 Å.

Recrystallisation of the crude product from the reaction in methanol from acetonitrile–diethyl ether gave the diethyl ether solvate $[Ag_2(bisox)_3](ClO_4)_2·Et_2O$ **2**. The asymmetric unit of **2** contains two partial silver atoms, with one-third occupancy, two independent ligand halves proximate to inversion centres,
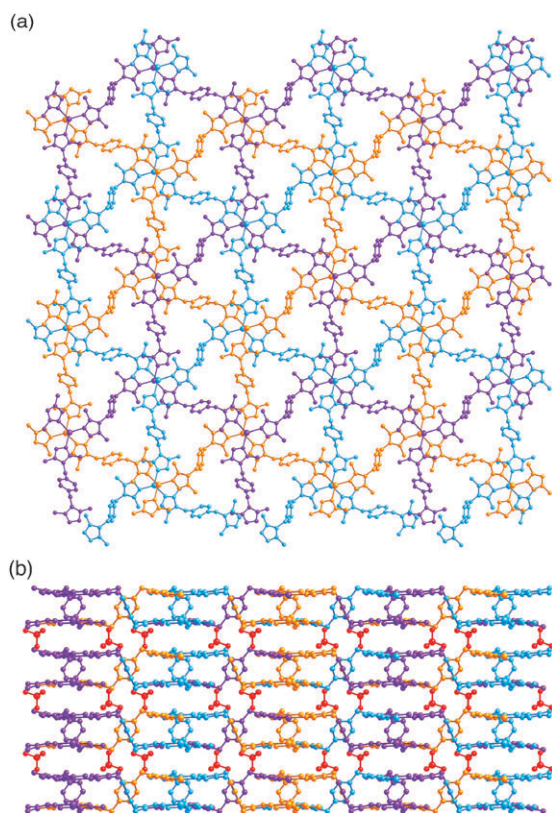
Fig. 2 The structure of $[Ag_2(bisox)_3](ClO_4)_2$ **1** showing (a) the triply interpenetrated network with the independent sheets shown in different colours, and (b) the position of the perchlorate ions, shown in red, between the interpenetrated layers.

two perchlorate fragments (central chlorines one-third occupancy) and a diethyl ether molecule with one-third occupancy. Both independent silver centres have trigonal planar geometry, each coordinated to three symmetry-related bisox ligands. However, the two independent bisox ligands have different conformations, with that coordinated to Ag(2) in the S-conformation, and that coordinated to Ag(1) in the C-conformation. As a consequence, Ag(2) forms triply parallel interpenetrated (6, 3) sheets similar to those observed in **1**, whereas Ag(1) forms discrete $Ag_2(bisox)_3$ cages, as depicted in Fig. 3a. The diethyl ether molecules project through the faces of these cages.

In the gross structure, the $Ag_2(bisox)_3$ cages lie directly above the silver centres of the interpenetrated sheets, as shown in Fig. 3b. As a consequence, there are two types of short Ag⋯Ag contact—those between the silver atoms within the sheets $[Ag(2)⋯Ag(2)'$ 3.0444(11) Å (Ag(2)$'$ generated by symmetry operation $x + 2, -y, -z + 1$)] and those between a silver atom in a sheet and a silver atom in a cage $[Ag(1)⋯Ag(2)$ 3.3253(8) Å]. The distance between the two silver atoms in a $Ag_2(bisox)_3$ cage is larger, at 8.004(1) Å. The perchlorate anions occupy positions to either side of the interpenetrated sheets, and are involved in C–H⋯O hydrogen bonds with CH donors on both the sheets and the cages.

The $Ag_2(bisox)_3$ cages are not observed in the absence of diethyl ether, and when the reaction is carried out in acetonitrile, only **1** is observed. The proximity of the Et_2O molecules to the cages in the structure of **2** implies that these molecules play a
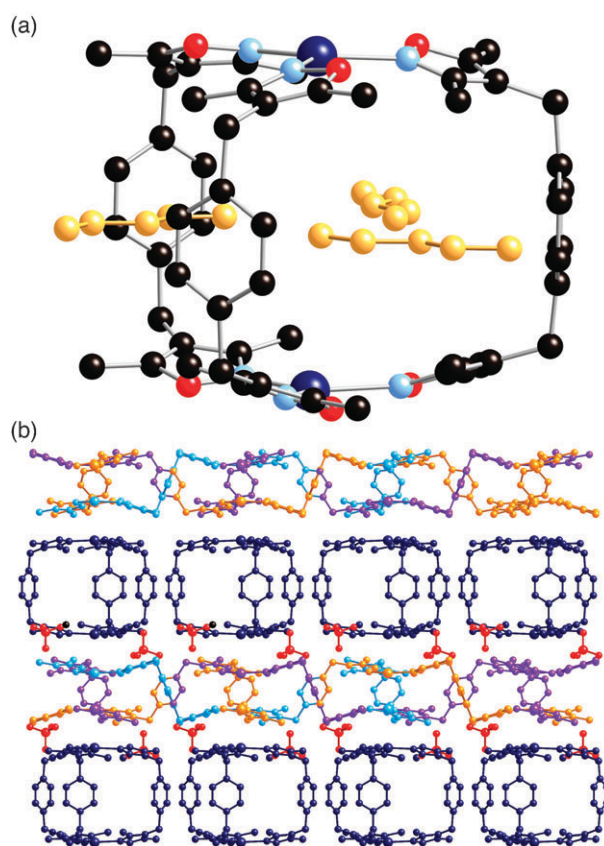

Fig. 3 The structure of $[Ag_2(bisox)_3](ClO_4)_2·Et_2O$ **2**, showing (a) the $Ag_2(bisox)_3$ cages, with the included diethyl ether molecules shown in orange, and (b) the alternation of triply interpenetrated sheets with rows of cages, shown in dark blue, with perchlorate anions shown in red. Hydrogen atoms have been omitted for clarity.

templating role in cage formation, and the data suggest the presence of C–H⋯O hydrogen bonds.

Given the similarity in formulae of **1** and **2**, and the correspondence in the relative positions of the silver centres in the two structures, we sought to investigate whether **2** could be converted to **1** by removal of diethyl ether, or whether desolvated cages could be obtained. No change was observed in the X-ray powder diffraction pattern of **2** on standing under vacuum for 4 h, or on heating at 50 °C under vacuum, but changes were observed when the sample was heated at 75 °C under vacuum (Fig. 4). On heating for 4 h, the sample slowly converted into **1**, as witnessed by changes in the X-ray powder
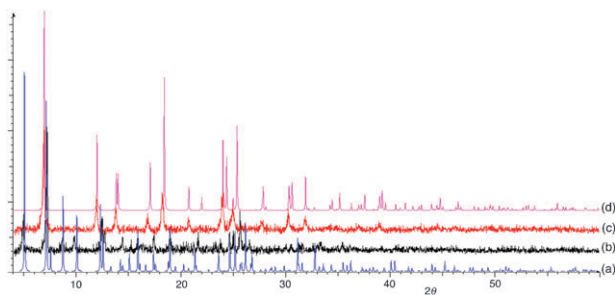

Fig. 4 Powder X-ray diffraction patterns for the conversion of **2** to **1**: (a) simulated pattern for **2**, (b) **2**, (c) **2** heated at 75 °C under vacuum for 1 h, and (d) simulated pattern for **1**.
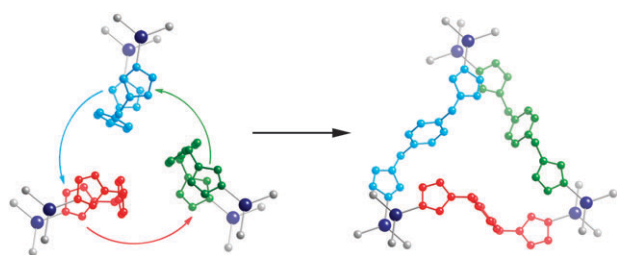
Fig. 5 The transformations required to convert the Ag₂(bisox)₃ cages in **2** into the triply-interpenetrated sheets in **1**.

diffraction pattern. These changes are consistent with complete and clean conversion of **2** to **1**. The TGA for **2** showed a mass loss of 2.7% between 100 and 120 °C which corresponds to removal of half of the diethyl ether (calc. for complete removal 5.4%). The remainder of the solvent is lost more gradually, with the network beginning to decompose at 280 °C.

The conversion of **2** to **1** is remarkable, given the extent of conformational reorganisation of the bisox ligands required. Conversion from the C-conformation in **2** to the S-conformation in **1** requires a rotation of 180° of one of the isoxazolyl rings about a methylene carbon atom which, in turn, involves the ring nitrogen atom moving through an arc of approximately 10.7 Å. This conformational change is accompanied by breaking and re-forming half of the Ag–N bonds, as shown in Fig. 5. Conversion of the cages into sheets also requires substantial movement of the silver centres, which is consistent with a shrinking along the c direction of 17%. Given this dramatic change in cell parameters between **2** and **1**, it is perhaps un-surprising that single crystals do not survive the transformation.

Rearrangement of coordination networks *via* dissolution–precipitation pathways is well established,[6] though solid state transformations are less common, and typically involve changes in the metal coordination environments.[7] Notably, interconversion between 1D, 2D and 3D silver–polynitrile coordination polymers have been shown to be promoted by anion exchange,[8] whereas conversion between 1D ladders and 2D bilayers in the [Zn₂(4,4′-bipy)₃(NO₃)₄] system has been facilitated by inclusion of guest molecules.[9] Dehydration of networks based on tris(carboxyethyl)isocyanurate[10] and 5-sulfoisophthalate[11] have both been demonstrated to initiate reversible transformations involving additional coordination of donor atoms from the ligands.

Further study of the transformation of **2** to **1** is currently underway, as is investigation of the reaction between bisox and other silver(I) salts.

Notes and references

‡ Synthesis of **1** and **2**: bisox (0.144 g, 0.49 mmol) was dissolved in methanol (10 cm³) with gentle heating and stirring. To this solution, AgClO₄ (0.050 g, 0.24 mmol) dissolved in methanol (3 cm³) was added. The product was allowed to crystallise overnight. This solid product was filtered and washed with methanol. Yield 0.146 g (93%). A crystal of **1** suitable for X-ray diffraction was obtained from the filtrate. Found: C, 49.54; H, 4.53; N, 5.91%. C₅₄H₆₀Ag₂Cl₂N₆O₁₄ requires C, 49.75; H, 4.64; N, 6.45%. The crude material from the methanol reaction was recrystallised by dissolving it in the minimum volume of CH₃CN and allowing Et₂O to slowly diffuse into the solution. Crystals of **2** of suitable size were produced for single crystal X-ray diffraction. Found: C, 50.60; H, 4.74; N, 6.09%. C₅₈H₇₀Ag₂Cl₂N₆O₁₅ requires C, 50.56; H, 5.12; N, 6.10%. Crystal data for **1**: $C_{54}H_{60}Ag_2Cl_2N_6O_{14}$, $M = 1303.72$, trigonal, $P\bar{3}$, $a = 14.8380(3)$ Å, $c = 7.3050(1)$ Å, $U = 1392.84(4)$ Å³, $T = 150$ K, $Z = 1$, 20 782 reflections collected of which 2127 are independent [$R_{int} = 0.0712$]. $R_1 = 0.0362$, w$R_2 = 0.0808$ for 1611 data with $I > 2\sigma(I)$. GOF = 1.052 based on F^2. Crystal data for **2**: $C_{58}H_{70}Ag_2Cl_2N_6O_{15}$, $M = 1377.84$, hexagonal, $P6_3/m$, $a = 14.4400(2)$ Å, $c = 35.3990(6)$ Å, $U = 6392.28(17)$ Å³, $T = 150$ K, $Z = 4$, 67 463 reflections collected of which 3828 are independent [$R_{int} = 0.1774$]. $R_1 = 0.0455$, w$R_2 = 0.1075$ for 2001 data with $I > 2\sigma(I)$. GOF = 0.937 based on F^2. The C–C and C–O distances within the diethyl ether molecule were restrained to being individually similar, and restraints were also applied to the associated atomic displacement parameters.

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