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Exploring the reversible host-guest chemistry of a crystalline octanuclear Ag(I) metallosupramolecular macrocycle formed from a simple pyrazinylpyridine ligand

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Here we report the synthesis of two new 2-(2′-pyrazinyl)pyridine ligands, and explore their coordination chemistry with Cu(II) and Ag(I) ions, leading to the discovery of metallosupramolecular architectures of suprising complexity. Differing only in the substitution pattern of a nitrophenyl substituent attached to the 4-pyridyl position, ligands **L1** and **L2** both form sulfate-bridged dinuclear complexes on reaction with copper sulfate, without coordination of the nitrogen atom at the pyrazine 4-postion. However, on reaction with Ag(I), both ligands adopt bridging coordination modes which lead to dramatically different outcomes. Ligand **L2** reacts with AgCF3SO3 to give a densely packed coordination polymer **3** of unusually low symmetry (*Z*′ = 7), while the structural isomer **L1** instead gives an octanuclear macrocycle **4** in the crystalline state. Macrocycle **4**, containing crystallographically-defined solvent molecules within its central cavity as well as in the interstitial spaces, readily undergoes solvent exchange in a single-crystal-to-single-crystal transformation. This allows a direct comparison of guest solvent affinity from single component and mixed-component exchange solutions using a combination of X-ray diffraction, NMR and TGA techniques, revealing the fully reversible uptake and exchange preferences of this material.

Introduction

The ongoing study of inclusion compounds and porous materials has led to many fundamental breakthroughs in our understanding of confinement and guest exchange phenomena in recent years.1,2 In particular, there has been a significant drive in the area towards developing dynamic properties of porous 3D materials that are responsive to guest inclusion, exchange or removal with retention of single crystallinity.3 This development lead to Fujita’s ground-breaking report in 2010 of the crystalline sponge method for structure determination within a coordination polymer.4 Recent results from a variety of fields intersect with studies of the ordered immobilization of guest molecules within a supramolecular host, for the subsequent exploitation of ordered confinement of guest molecules.5 These can take the form of, for example, topochemical polymerisations,6 chemical sensing,7 and photochemistry of confined species.8 A constant driving force in this area is the ever-present need for chemical diversity; expanding the lessons learned on the early generation of porous hosts into ever more complex self-assembled systems.9

The careful manipulation of reaction conditions and the concept of directional molecular self-assembly is critical in the rational design and construction of such assemblies. Furthermore, when choosing an appropriate metal ion the intrinsic reversibility in the formation of metal-ligand bonds is also essential.10 Ag(I) is a popular choice of metal ion for crystal engineering when investigating the nature of crystalline metal-organic assemblies.11 Although not generally renowned for robust porous coordination networks, it lends itself to flexible coordination and lability towards soft electron donors by virtue of its inherent soft Lewis acid character.12 Moreover, a wide variety of architectures can be generated due to the absence of strongly preferred coordination numbers and geometries.



**Scheme 1** Structure of ligands **L1** and **L2**

In some instances, the flexible coordination geometry of Ag(I) can act as a structural hinge for dynamic porosity in flexible porous crystals, which has been used to study guest uptake phenomena and the subsequent impact on the host material.13 Herein, we present the synthesis and coordination chemistry of two novel pyrazinylpyridine (*PzPy*) hybrid ligands, **L1** and **L2** respectively. These ligands act as scaffolds in the synthesis of four distinct and fluxional supramolecular architectures using Ag(I) and Cu(II) ions. Our results reveal fascinating insights into the structural chemistry and the reversible guest exchange properties of a crystalline self-assembled octanuclear macrocycle. Moreover, we provide a direct comparison of the exchange affinity in solution with various solvent guests, by using the combination of NMR, TGA and critically, X-ray diffraction experiments, of Ag(I) coordination material.

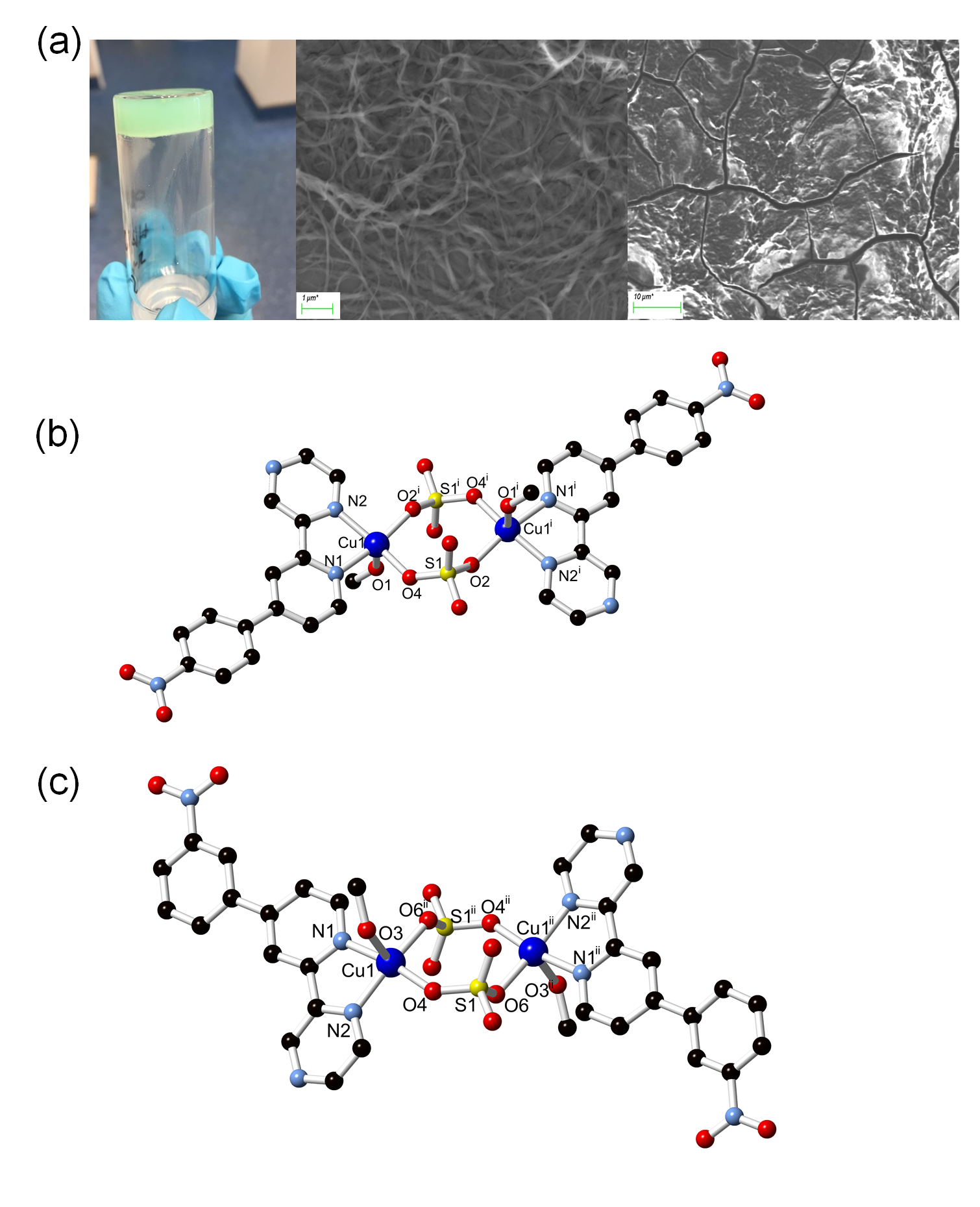
Results and Discussion

Ligands **L1** and **L2**, shown in Scheme 1, were prepared by modified literature procedures14 substituting the classic “Kröhnke reagent” 2-pyridacyl pyridinium iodide15 for the novel pyrazine equivalent in order to install an additional coordinating site on the outer heterocycle. The appropriate 4- or 3-nitrobenzaldehyde was reacted with sodium pyruvate to generate the precursor chalcone, which was subjected to a Kröhnke-type pyridine synthesis with 2-pyrazinacyl pyridinium iodide and ammonium acetate in H2O to yield the carboxylate precursors of **L1** and **L2** as their ammonium salts. These intermediates were directly subjected to thermal decarboxylation to give the ligands **L1** and **L2**.The crystal structure of 2-pyrazinacyl pyridinium iodide was fortuitously obtained during the synthesis, confirming the expected structure and being largely consistent with the pyridine equivalent (ESI, Figure S1).16

**Synthesis and Structure of copper(II) sulfate complexes of L1 and L2**

In order to gauge the physical dimensions and coordination preferences of the new ligands in simple systems, each ligand was reacted with copper(II) sulfate, with the expectation of generating simple discrete complexes. In both the cases of **L1** and **L2**, carrying out this reaction in methanol gave a green amorphous material, which subsequently underwent crystallization over the course of several days.

In the case of **L1**, the flocculent material was only loosely associating, and readily dispersed into the supernatant. However, the material formed by **L2** was considerably more robust, able to support its own weight as a freestanding gel monolith and resistant to an inversion test, as is demonstrated in Figure 1a. This soft material was formed within 3 hours either at room temperature or at 1-2 °C, at 9 mM concentration of the two components (*ca.* 0.5 wt%). The “Cu-**L2**” material exhibits a fibrous morphology upon imaging with scanning electron microscopy (SEM), similar to typical supramolecular gel materials and shown in Figure 1(a).17 Examination of the material using thermogravimetric analysis (TGA) showed a



**Figure 1** The structure and properties of complexes **1** and **2**; (a) The flocculent material obtained from the initial reaction of **L2** with copper sulfate (left). SEM images of the material deposited from a fresh sample (middle) and a sample after three days (right); (b) Structure of complex **1** with partial atom labelling scheme; (c) Structure of complex **2** with partial atom labelling scheme. All hydrogen atoms and lattice solvent molecules are omitted for clarity. Symmetry codes used to generate equivalent atoms: (i) -x, 1-y, -z; (ii) 1-x, 2-y, 1-z.

residual non-volatile mass between 1.8 – 2.0 %, alluding to the loose nature of the gelatinous material and the presence of non-encapsulated solvent on the particle surfaces. Over the course of 96 hours the material subsequently acted as a crystal growth medium and led to the formation of blue crystals and a colourless supernatant. Further SEM analysis of the soft material after 48 hours showed that the material exhibits a rougher texture than the freshly prepared sample, coinciding with occurrence of crystal nucleation.18

The blue-green block crystals deposited from their flocculent or gelatinous precursors analyzed for the formulae [Cu2**L1**2(SO4)2(CH3OH)2] **1** and [Cu2**L2**2(SO4)2(CH3OH)2] ·2CH3OH·1H2O **2**. Single crystals of **1** were formed at room temperature whereas diffraction-quality single crystals of **2** were obtained from a mixture left to stand at 1-2 °C. The major fragments of both complexes are chemically equivalent, as shown in Figure 1(b) and (c), with complex **2** crystallising as a mixed H2O/MeOH solvate. The complex consists of two equivalent five-coordinate copper(II) ions bridged by two sulfate anions into a centrosymmetric 8-membered ring. In both cases, the copper ions adopt well-defined square pyramidal coordination geometries, completed by one chelating **L1**/**L2** molecule per copper ion and an axially oriented methanol ligand. Intramolecular (6) hydrogen bonding interactions are evident between the methanol ligand and non-coordinating sulfate oxygen atoms in **1**, while the slightly different 8-membered ring conformer in **2** enforces a similar intermolecular (12) interaction.

In similar cobalt(II)/(III) and cadmium(II) complexes we have recently reported prominent C-H···O and anion···π-hole interactions within the extended structures.19 In the case of **1** and **2**, similar interactions are evident from the “bay” of inward facing aromatic C-H groups (crystallographic labels C3, C6 and C11) which donate hydrogen bonds to a non-coordinating sulfate oxygen atom. Each of the C···O distances fall within the range 3.214(7) to 3.661(2) Ǻ, and all six C-H···O angles lie between 154.618(19) and 173.6(3)°.20 The O5 oxygen atom also accepts a hydrogen bond from the oxygen atom O1 of the coordinating methanol group with an O···O distances of 2.61363(17) and 2.707(5) Ǻ as well as O-H···O angles of 154.024(2) and 159.000(4) ° for **1** and **2**, respectively.

**Synthesis and Structure of polymeric Ag complexes with L1 and L2** *Structure of poly-[Ag7****L2****7]7(CF3SO3)****3*** *and* *[Ag­8****L1****8]8(CF­3­SO3)·8C3H6O* ***4***.

With the expectation that a softer metal ion would encourage bridging through the pyrazin-4-yl nitrogen atom, we turned our attention to Ag(I) as a suitable soft Lewis acid for these studies. Pale yellow block crystals suitable for analysis by single crystal X-ray diffraction formed from a mixture of **L2** and silver trifluoromethanesulfonate in acetone. The single crystal X-ray diffraction data for *poly*-[Ag7**L2**7]7(CF3SO3)**3** were solved and refined in the monoclinic space group *Cc.* No indication was detected of the higher symmetry *C*2/*c* setting, either in terms of systematic absences or a feasible solution.

The asymmetric unit of **3** contains seven unique molecules of **L2**, seven Ag ions, and seven triflate counterions (Figure 2); this rare example of *Z*′ = 7 can be rationalized by the diversity of coordination modes present within the structure. All seven **L2** molecules bridge two silver ions, coordinating in a chelating fashion through the pyridyl and pyrazin-1-yl nitrogen atoms, and in a monodentate fashion *via* the pyrazin-4-yl nitrogen atom. Three of the seven unique silver ions are bound in N4 *pseudo-*square-planar geometries by two chelating **L2** species. Within these coordination spheres, the Ag-N bonds from the pyridyl nitrogen atoms are consistently *ca*. 0.2 – 0.3 Å shorter than those involving the pyrazin-2-yl nitrogen atoms, consistent with both the reduced σ-donor ability of pyrazine compared to pyridine, and its µ2 coordination mode. Another three unique silver ions adopt linear 2-coordinate geometries, bound by two monodentate pyrazin-4-yl nitrogen atoms, with additional close contacts to triflate oxygen atoms (with Ag···O distances in the range 2.468(11) – 2.695(15) Å measuring *ca*. 0.2 – 0.5 Å longer than the Ag-N bonds).

Crucially, the final unique silver ion adopts a third coordination geometry, a T-shaped 3-coordinate geometry, with coordination sites occupied by one bidentate **L2** chelate and one monodentate **L2** pyrazin-4-yl donor. This coordination site also fits the trend described above of more strongly bound *trans* pyridyl and pyrazin-4-yl donors (Ag-N distances 2.283(11)



**Figure 2** Structure of the repeat unit and seven unique silver ions in the structure of **3**. Hydrogen atoms and triflate anions are omitted for clarity. Symmetry codes used to generate equivalent atoms: (i) 3/2+x, 1/2-y, z-1/2; (ii) x-3/2, 1/2-y, 1/2+z.

and 2.273(12) Å, respectively) and a weakly bound pyrazin-2-yl donor (Ag-N distance 2.508(12) Å). The outer coordination sphere of Ag7 exhibits further weak interactions with nearby triflate oxygen atoms, with the shortest Ag···O distance 2.647(16) Å for Ag7-O31. When considering only the Ag-N connections as the most significant interactions within the structure, the extended structure of complex **3** can be described as a one-dimensional coordination polymer. The geometry of the repeat unit is dictated by the alternating geometries of the silver sites; linear segments consisting of the six alternating 2-coordinate and 4-coordinate centers are interrupted by corners defined by the 3-coordinate Ag7 site. This arrangement results in a zig-zag extended structure with corner (Ag···Ag···Ag) angles of 92.609(4)° and a very large linear distance between corners (defined as Ag7 sites) of 51.2276(17) Å.

These one-dimensional polymeric assemblies are linked into a densely packed three-dimensional array through a variety of bridging interactions between adjacent silver ions. Several triflate counterions are involved in weak µ2-κO:κO′ bridging between adjacent silver ions, and an argentophilic interaction is present between silver atoms Ag1 and Ag3, at a Ag···Ag distance of 3.1466(18) Å. Various other close contacts between adjacent silver ions are also present at separations slightly beyond the sum of the van der Waals radii (*ca.* 3.44 Å).21 By virtue of these and other weak bridging modes of the triflate counterions, the silver ions align in stacks with an offset to the propagation axis of the one-dimensional zig-zag polymer (Figure 3), leading to dense three-dimensional inter-chain connectivity. In a similar manner to the previously described complexes, various C-H···O hydrogen bonding interactions are evident originating from the 3-pyridyl and 3-pyrazinyl C-H groups with additional contributions from the nitrophenyl ring. These interactions terminate with triflate oxygen atoms or nitro groups from adjacent molecules. Pleasingly, no notable crystallographic disorder was detected in the orientation of any of the triflate anions or the main residue atoms. No solvent molecules or additional encapsulated guests were detected within the structure, and no meaningful void volume was present.



**Figure 3** Three adjacent 1-dimensional chains in the structure of **3** coloured separately and showing the alternating overlapping and staggered arrangement of the linear segments. Hydrogen atoms and anions are omitted for clarity.

Having determined and rationalized the structure of **3**, complex **4** was prepared under analogous conditions, differing only in the substitution pattern of the nitrophenyl substituent at the pyridyl 4-position. Pale yellow single crystals of **4** were analyzed by single crystal X-ray diffraction, and the diffraction data were refined in the triclinic space group *P*-1. The asymmetric unit of **4** contains four silver ions and associated triflate counterions, four molecules of **L1**, five lattice acetone molecules and one partial-occupancy aqua ligand. In general terms, the structure of **4** draws a strong parallel to complex **3**; both frameworks adopt the empirical formula [Ag(**L**)(CF3SO3)]n, and both structures contain a combination of 2-, 3- and 4-connected silver ions when considering only N-donor ligands, with further weak association of triflate anions. For the purposes of simplicity, the myriad weak Ag-O interactions involving the triflate anions are largely excluded from this discussion, as these fall in a continuum of distances from 2.475(2) Å upwards and involve significant contributions from disordered anions which do not make a meaningful contribution to the topology of the structure.

Key geometric differences in the coordination geometry in **4**, however, give rise to a remarkable difference in extended structure. In **4**, silver ions Ag1 and Ag2 act as essentially linear linkers between molecules of **L1**, adopting linear 2-coordinate and Y-shaped 3-coordinate geometries, respectively. For Ag1, both donors consist of pyrazin-4-yl nitrogen atoms, while Ag2 is chelated by one **L1** molecule and capped by a pyrazine-4-yl nitrogen atom. Surprisingly, in comparison to complex **3**, the pyrazine groups provide the shorter Ag-N distances in this case, of 2.286(2) and 2.190(2) Å for N6 and N11, respectively, compared with 2.349(2) Å for N5. In the cases of Ag3 and Ag4, crucial discrepancies from the structure of **3** are revealed, as these silver ions both adopt coordination geometries leading to bending or twisting features in the superstructure. Silver ion Ag3 adopts a 4-coordinate, bis-bidentate geometry, with an angle of 81.06(4)° relating the two divergent pyrazin-4-yl donor atoms to the central silver ion (compared with angles of *ca.* 160-170° for the related 4-coordinate silver ions in complex **3**). Meanwhile, Ag4 is coordinated by a bidentate **L1** molecule, a monodentate pyrazin-4-yl nitrogen atom, and weakly bound by a triflate oxygen atom, again angling the divergent donor atoms from this corner at a 104.96(4)° incline. Rather than the polymeric structure observed in **3**,the convergent structural feature presented by virtue of the Ag3 and Ag4 node geometries gives rise to a closed cyclic assembly in **4**; specifically, an octanuclear metallomacrocycle of the formula [Ag8(**L1**)8]8(CF3SO3) shown in Figure 4.



**Figure 4** Structure of complex **4**; (a) The asymmetric unit of **4** with labelling scheme for coordinating heteroatoms; (b) the complete structure of the metallomacrocycle **4**. All hydrogen atoms, anions and solvent molecules are omitted for clarity. Symmetry codes used to generate equivalent atoms: (i) 1-x, 1-y, -z.

The macrocycle itself adopts a flattened parallelepiped shape, with a central cavity of interatomic dimensions *ca*. 7 × 17 Å. In the crystallographic model, this centrosymmetric cavity fully encapsulates two triflate anions, two acetone molecules and includes two partial-occupancy aqua ligands (total occupancy 1.5). Adjacent macrocycles in the structure of **4** associate primarily on the flattened faces through electrostatically bound weakly bridging triflate groups, most of which exhibit Ag-O distances in excess of 2.7 Å (Figure 5). While several Ag···Ag contacts are evident, even the shortest of these (3.4948(5)) Å for Ag2···Ag4) falls beyond the formal criterion for significant argentophilic interactions.22 The extended π-system also contributes to the overall crystal packing through various face-to-face π-π interactions, shown in Figure 5. Despite the lack of strong connectivity between adjacent macrocycles, the extended structure of **4** results in alignment of macrocycles such that their central cavities form continuous one-dimensional channels, oriented parallel to the crystallographic *b* axis. As well as the acetone molecules and aqua ligands located near the center of the main cavity, further pockets of lattice solvent molecules and are located at the periphery of these channels between adjacent macrocycles. All in all, the crystallographic model suggests that the freshly isolated crystals of **4** contain approximately ten acetone molecules per macrocycle, all of which being accessible from continuous channels.



**Figure 5** (a) The weak triflate-mediated linkages between the outer faces of the macrocycles in complex **4**; (b) The extended structure of **4** with a single macrocycle highlighted in green, showing the crystal packing modes normal to the macrocycle face (top) and in an orthogonal direction (bottom). All hydrogen atoms, solvent molecules and anions are omitted for clarity. Symmetry codes used to generate equivalent atoms: (i) x-1, +y, +z

Guest Exchange properties of 4

The presence of a substantial quantity of potentially mobile guest molecules within **4** prompted an investigation into its guest exchange functionality. In the first instance, and for comparison with the crystallographically disordered guest molecules, crystals of **4** were decomposed in *d*6-DMSO, and 1H NMR was used to quantify the total guest loading in the bulk sample. The value obtained by this method of 6.7 molecules of acetone per macrocycle was broadly consistent with the value obtained by thermogravimetric analysis (observed 8.7% mass loss between 0-200 °C, calculated by NMR 8.3 %). Perhaps unsurprisingly, given the crystallographic disorder and well-known difficulties in accurately quantifying disordered solvent molecules within continuous channels,23 this quantity is smaller than that observed crystallographically (calc. 11.9%). As thermogravimetric analysis revealed the guest acetone molecules were readily and completely removed, and followed by a broad plateau before thermal decomposition, a sample of **4** was evacuated under dynamic vacuum at 90 °C for 24 hours before being examined for gas uptake properties. However, negligible adsorption of N2 (77 K) or CO2 (278 K) was observed (ESI, Figure S33 and S34), suggesting a contraction or collapse of the structure of **4** when completely evacuated.

In order to test the properties of **4** with respect to guest exchange under less forcing conditions, single crystals of the complex were taken from the acetone mother liquor and immediately soaked in a variety of common organic solvents. After 24 hours at room temperature, no change was evident in the colour, size or morphology of the crystals, and X-ray powder diffraction revealed the crystallographic symmetry and unit cell parameters of the exchanged materials to be retained. Each batch of crystals was filtered and digested with *d*6-DMSO to screen the degree of solvent exchange; as shown in Table 1, in general smaller or more polar guests were able to fully displace the lattice acetone molecules (tetrahydrofuran, 1,4-dioxane and ethyl acetate), while others, which were larger or more lipophilic resulted in only partial exchange (benzene, toluene, hexane and carbon tetrachloride), giving materials containing a mixture of the original lattice acetone and the soaking solvent. This observation is uniformly in line with the polarity index of the exchange solvents.24

By 1H NMR (400 MHz) analysis the adsorbed quantity of the soaked guest relative to residual acetone was >95% for the fully exchanged samples, compared to 14 – 82 % for the incompletely exchanged samples (benzene > toluene > hexane). Adsorption of stronger donor solvents (acetonitrile, quinoline and benzonitrile) resulted in the destruction of the crystalline **4**. Given the preferential adsorption of benzene compared to hexane, solutions of naphthalene dissolved in either ethyl acetate (2 mL) or hexane (2 mL) were also investigated, however these experiments only showed uptake of the carrier solvent by NMR. Pleasingly, the crystals of **4** retained sufficient single crystallinity for their structure determinations to be repeated in the presence of the exchanged guests. In each case, related unit cell parameters were obtained, and the chemical nature of the framework itself was, to a great extent, unchanged.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Compound** | **Guests per macrocycle from NMRc**  **(Soaked/ Acetone)** | **Guests per macrocycle from SCXRD**  **(Soaked/ Acetone)** | **% Soaked per total guests (NMR/ SCXRD)** | **% Mass loss measa / calc (NMR) / calc (SCXRD)** |
| **4 (acetone)** | - / 6.7 | - / 10 | 100/100 | 8.7 / 8.3 / 11.9 |
| **EtOAc⊂4** | 4.3 / <0.1 | 7/0 | >95/100 | 13.1 / 8.1 / 12.6 |
| **Dioxane⊂4** | 3.6 / <0.1 | 6.2/0 | >95/100 | 10.9 / 6.9 / 11.3 |
| **THF⊂4** | 2.8 / <0.1 | 6.5/0 | >95/100 | 10.3 / 4.5 / 9.9 |
| **C6H6⊂4** | 0.9 / 0.2 | 3.5/3.5 | 82/50 | 10.8 / 1.9 / 10.0 |
| **PhMe⊂4** | 2.9 / 2.1 | 2.7/3.5 | 58/44 | 10.5 / 8.3 / 9.6 |
| ***n-*Hexane⊂4** | 0.8 / 4.7 | 1/8 | 14/11 | 11.7 / 7.4 / 11.4 |
| **CCl4⊂4** | N/A / 6.3 | 2/8 | -b/20 | 11.4 / -b / 15.2 |

**Table 1** Summary of exchange properties of **4** comparing the calculated solvent loadings (molecules per macrocycle) obtained by SCXRD and NMR, and the measured (TGA) and predicted volatile masses in %. aTotal volatiles lost below 200 °C; bNot determined; cError associated with NMR solvent integrals *ca.* 10%

For each structure the exchange solvent could be located from Fourier residuals within the central cavity of the macrocyclic species, as exemplified in Figure 6. The solvents which exhibited greater tendencies to strongly displace the lattice acetone molecules could also be located in additional sites within the lattice, with varying degrees of crystallographic disorder evident as functions of both the geometry and symmetry of the guest species and the presence of any defined interactions within the framework. For example, in the case of 1,4-dioxane, weak Ag-O coordination was observed at the two-coordinate Ag1 site. This position within the macrocycle allows the solvent to partially localize in a weakly metal-coordinating position displaying an Ag···O distance of 2.695(8)Å. While the total degree of solvation ascertained by SC-XRD was uniformly larger than that observed by NMR, the relative ratio of guests in the case of mixed-guest systems was broadly comparable between the two techniques.

Although the unit cell volumes vary in the range 4565.4 – 4753.8 Å3 from the smallest (PhMe) to the largest (THF), a variance of *ca*. 4%, correlations between these parameters and the physical properties of the guest solvents are not obvious. No clear correlation between the unit cell volume and electronic parameters (dipole moment, polar surface area, logP, dielectric constant) or molecular volume of the guests can be easily drawn. Indeed, the unit cell volume is not correlated to the total molecular volume of the guest molecules, implying slight rearrangements of the host molecules beyond simply incorporating the guests. The variations in unit cell volume, in comparison to the original acetone structure, tend to manifest as contractions along *a* and *c* with concurrent expansions along *b*. The THF-exchanged material is the only compound to expand along all three axes compared to the pristine **4**, while benzene shows the greatest fractional variation of all three axes, increasing in *b* by *ca.* 6% with contractions in *a* and *c* of approximately 3.5% (ESI, Tables S2-S3).

Thermogravimetric analysis (TGA) was also conducted to further quantify the amount of solvent encapsulated within **4**. Interestingly, the mass losses recorded in the range 30 – 200 °C for essentially all materials bar the original compound **4** and the CCl4 exchanged sample show excellent agreement (within 0.9 %) with the values calculated from the solvation modelled in the single crystal structures of each compound. However, the total solvation estimated from NMR was uniformly lower than that observed from both SC-XRD and TGA. This discrepancy is most likely explained by the rapid onset of mass loss in the materials; while both SC-XRD and TGA measurements could be carried out immediately on removal of the crystals from the mother liquor, some volatiles may have been more readily lost during filtration and digestion of the solids for NMR analysis. While the fully-exchanged materials all exhibited similar mass loss profiles with rapid initial mass loss shallowing above 100 °C, partial exchange with the non-polar toluene, benzene, carbon tetrachloride and hexane guests gave additional well-defined mass loss steps at *ca*. 150 °C, indicating a more complex desolvation process for the mixed-guest systems.



**Figure 6** Representative positions of solvent molecules within the central cavity of macrocycle **4**, showing acetone molecules and aqua ligands (top) and dioxane molecules (bottom). Both disordered orientations of the innermost dioxane guest are shown overlapping. All hydrogen atoms, anions and solvent molecules residing outside of the central cavity are omitted for clarity.

Given the clear differentiation in guest affinity shown between polar and non-polar guests, the relative affinities of the fully exchanged guests (1,4-dioxane, THF and ethyl acetate) were also investigated. Using 1:1 solvent mixtures as exchange media and comparing the relative integrals of the guests in the digested material by NMR (ESI, Figure S23-25), preferential adsorption of one component was observed, showing a trend in affinity of 1,4-dioxane>EtOAc>THF (Table 2).

|  |  |
| --- | --- |
| **Soaking Mixture** | **Guest Content** |
| **1: 1** 1,4-dioxane: THF | **2.2: 1** 1,4-dioxane: THF |
| **1: 1** 1,4-dioxane: EtOAc | **1.2: 1** 1,4-dioxane: EtOAc |
| **1: 1** THF: EtOAc | **2.0: 1** EtOAc: THF |

**Table 2** The guest content, ascertained by digestion and NMR, of complex **4** samples following exposure to solvent mixtures.

As single crystallinity was retained throughout the exchange process, we also investigated the effect of re-immersing an exchanged sample in acetone, to revert to the original structure. The crystals of **1,4-dioxane⊂4**, the most preferentially absorbed guest observed, were re-soaked in the original synthesis solvent acetone (4 mL). The twice-exchanged crystals, **acetone⊂**(**1,4-dioxane⊂4)** were then subjected to further single crystal X-ray diffraction experiments. While little change was observed in the morphology of the crystals there was an obvious decrease in the diffraction quality, with no useful reflections observed beyond 0.83 Å resolution (Mo Kα). Nevertheless, from these data a crystallographic model could be generated which confirmed the presence of five unique acetone sites within the asymmetric unit, having completely displaced the ordered 1,4-dioxane guests, and completely regenerating the original arrangement. Interestingly, the partial-occupancy aqua ligand present in the original structure of **4** was also recovered. While no 1,4-dioxane was detected from the Fourier residuals in this experiment, further 1H NMR analysis of the digested bulk sample in *d*­­­6-DMSO revealed a small quantity of 1,4-dioxane (approximately 1:12 dioxane:acetone, ESI Figure S22), implying that trace amounts of the initial exchange solvent is retained within the sample. X-ray powder diffraction (ESI, Figure S14) confirms full recovery of the original phase, most indicative from regeneration of the defined peak profiles for the low angle reflections. This reversibility experiment is indicative of the structural resilience of the system; although the porous nature of **4** was not detected upon solvent evacuation, the crystalline macrocycle is clearly capable of sequential and reversible guest exchange.

Conclusions

We have prepared and structurally characterised four new *d*-block metal complexes from the 4- and 3- isomers of a pyrazinylpyridine ligand scaffold, **L1** and **L2**. In the case of copper sulfate pentahydrate with both **L1** and **L2** the initial formation of a green gel-like material acted as a crystal growth medium for mononuclear complexes **1** and **2**, each containing two equivalent Cu(II) ions bridged by sulfate anions; two structures which were functionally equivalent, independent of the ligand substitution pattern. In the case of Ag(I), however, these minor geometric differences between **L1** and **L2** gave rise to two remarkably distinct crystalline superstructures. For **L2** the reaction in acetone gave rise to a one-dimensional polymer **3**, in which three distinct coordination geometries for Ag(I) led to a zig-zag coordination polymer with *Z*′ = 7 and a distance of over 50 Å between corners.

Conversely, the reaction of the 4-isomer **L1** gave an octanuclear metallomacrocycle **4**, which contained acetone molecules both encapsulated within the void of the macrocycle and present within the periphery between neighbouring macrocycles. Guest exchange experiments with seven different guests, as well as mixtures of guests and sequential exchanges, showed **4** undergoes reversible single-crystal-to-single-crystal transformations. Most importantly, the guest molecules occupy crystallographically defined positions within the macrocycle which could be individually located and correlated well to the bulk solvation ascertained by TGA. These results show that surprisingly diverse and intricate functional coordination architectures can be realised from simple building units with seemingly minor geometric variations, and that the potential functionality of such materials in guest exchange applications can be accessed without the necessity for robust 3-dimensional frameworks.

Experimental Section

**Materials and Methods**

The chalcone precursors were synthesised according to literature procedures.25 (ESI) All other reagents and solvents were purchased from Sigma-Aldrich, Merck or Fisher Scientific, were of reagent grade or better, and were used as received. All NMR spectra were recorded using either a 400 MHz Bruker Avance III or 600 MHz Bruker Avance II spectrometer, operating at 400.1/600.1 MHz for 1H NMR and 100.2/150.2 MHz for 13C NMR. Chemical shifts are reported in ppm referenced relative to the internal residual solvent signals. Electrospray mass spectra were recorded on a Micromass LCT spectrometer or a MALDI QToF Premier, running Mass Lynx NT V 3.4 on a Waters 600 controller connected to a 996 photodiode array detector with HPLC-grade methanol or acetonitrile. High resolution mass spectra were determined by a peak matching method, using leucine enkephaline (Tyr-Gly-Gly-Phe-Leu) as the standard reference (*m/z* = 556.2771). All accurate masses were reported within ±5 ppm. Melting points were determined using an IA9000 digital melting point apparatus in air and are uncorrected. Infrared spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer fitted with a Universal ATR Sampling Accessory. Elemental analyses were carried out at the Microanalytical Laboratory, School of Chemistry and Chemical Biology, University College Dublin and The Department of Chemistry, Maynooth University. Thermogravimetric analysis was performed using a Perkin-Elmer Pyris 1 TGA instrument, with samples (1 – 5 mg) mounted in alumina pans and heated in the range 25 – 500 °C at a rate of 5 °C/min under a constant N2 flow of 20 mL/min**.** Gas adsorption isotherms were measured using a Quantachrome Autosorb IQ gas sorption analyser. Chemically pure (CP, N4.5) grade He, N2 and CO2 gases from BOC gases were used for the measurements.

**Synthesis**

**[Cu2L12(SO4)2(CH3OH)2] (1)**

Copper(II) sulfate pentahydrate (9 mg, 0.036 μmol) was dissolved in MeOH (2 mL) and added to a sonicated suspension of **L1** (10 mg, 0.035 μmol) in MeOH (2 mL), and the mixture was sealed. A flocculent green precipitate formed immediately, which was converted to green crystals after 72 hrs. These crystals were isolated by filtration. The crystals of **1** tended to lose crystallinity and adsorb atmospheric water over time after drying in air. Yield 5 mg, 30 %; m.p. 280-300 °C (decomp.); νmax (cm-1) 3041m br, 1609m sh, 1551m sh, 1520m, 1514m, 1477w, 1408m sh, 1345s sh, 1175w, 1139m, 1093s, 1054w, 1046s, 972m, 931w br, 846m sh, 824m sh, 752m sh, 749w, 691w, 615m br; Found C, 37.28; H, 3.14; N, 11.65%. C30H20Cu2N8O12S2·5H2O requires: C, 37.30; H, 3.13; N, 11.60%**.**

**[Cu2L22(SO4)2(CH3OH)2]·2CH3OH·H2O (2)**

Copper(II) sulfate pentahydrate (9 mg, 0.036 μmol) was dissolved in MeOH (2 mL) and added to a sonicated suspension of **L2** (10 mg, 0.035 μmol) in MeOH (2 mL). The mixture was sealed andcooled at 1-2 °C. After 3 hrs, green gelatinous material is evident, which converts to green/blue crystals after 72 hrs, which were isolated by filtration. The crystals of **2** tended to adsorb atmospheric water over time after drying in air.

Complex **2**: Yield 11 mg, 65%; m.p. 250-270 °C (decomp) ; νmax (cm-1) 3233m br, 1614m sh, 1529m sh, 1510w, 1490w, 1407,m sh, 1349m sh, 1174w, 1150w, 1050w, 1035w, 1014s sh, 990w, 910m, 852w, 815m sh, 732m sh, 674m, 606s, 590s; Found C, 34.97; H, 3.67; N,10.93. C30H20Cu2N8O12S2·9H2Orequires C, 34.71%; H, 3.69%; N, 10.79%

Xerogel: 8 mg isolated; m.p > 300 °C (decomp); νmax (cm-1) 3012w br, 2983w, 1613m sh, 1527m sh, 1519w, 1467w, 1409m sh, 1353m sh, 1295w, 1107w, 1090s br, 1065w, 995m sh, 945m br, 853w sh, 785w, 751w, 723w, 716w, 667w, 672w, 619s sh; Found C, 37.05; H, 2.75; N, 11.35%. C30H20Cu2N8O12S2·5H2O requires C, 37.3, H, 3.31, N, 11.6%.

***poly*-[Ag7L27]·7CF3SO3 (3)**

Silver trifluoromethansulfonate (9 mg, 0.035 μmol) was dissolved in acetone (2 mL) *via* sonication and added to a solution of **L2** (10 mg, 0.035 μmol) in acetone (2 mL). The reaction was sealed to stand at room temperature with light excluded for 48 hrs, after which time the colourless crystals were isolated by filtration. Yield 7 mg, 37%; mp 229-230 °C (decomp); νmax (cm-1) 3482w br, 3081m br, 1980s, 1607m sh, 1527s sh, 1474m, 1409m sh, 1348s sh, 1237s br, 1222s br, 1153s sh, 1109w, 1072w, 1023s sh, 896w, 847m sh, 807m, 799m, 735m, 689m sh, 631s sh 572m sh; Found C, 35.89; H, 1.97; N, 10.28%. C112H70Ag7F21N28O35S7 requires: C, 35.90; H, 1.88; N, 10.46%.

**[Ag8L18]8CF3SO3·10C3H6O (4)**

Silver trifluoromethansulfonate (9 mg, 0.035 μmol) was dissolved in acetone (2 mL) *via* sonication in a glass vial and added to a solution of **L1** (10 mg, 0.035 μmol) in acetone (2 mL). The reaction was sealed and light was excluded. The reaction was left at room temperature for 48 hrs after which time a crop of yellow crystals formed in pure phase. Yield 12 mg, 56%; m.p. 165-188 °C (decomp); νmax (cm-1) 3469w br, 3079w, 1704m sh, 1609m sh, 1598m sh, 1553m sh, 1519m sh, 1479w, 1415m sh, 1395m sh, 1348s sh, 1228s, 1212s, 1155s sh, 1075w, 1110w 1021s sh, 1011w, 909w, 859m br, 843m sh, 831m sh, 754m sh, 684m, 655m shs; Found C, 33.29; H, 1.84; N, 9.06%. C67H40Ag4F12N16O20S4 +4.5 C­3H6O + 0.75 H2Orequires: C, 33.31; H, 1.98; N, 9.27%.

Conflicts of interest

There are no conflicts to declare.

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