An unusual harmonisation of metal-based assemblies to achieve a mesoporous solid. Synthesis and crystal structure of a new silver(I) isonicotinate array

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The synthesis and crystal structure of a novel silver(I) mesoporous material are reported. The crystal structure is built from two different 1-D metal-based assemblies. A discrete [Ag(HIso)(Iso)] (HIso = isonicotinic acid) complex assembled *via* charge-assisted O···H···O hydrogen bonds co-exists with a $[Ag(Iso)]_n$ co-ordination polymer. Both 1-D arrays are essentially sustained together through π–π and Ag···O intermolecular interactions. This crystal structure is an illustrative example of an unusual harmonisation of different metal-based assemblies to achieve a new supramolecular architecture.

The possibility of accessing new solid materials with pre-designed properties has meant that scientists from different fields have directed special attention to crystal engineering. This field of material science concerns, precisely, the development of protocols for controlling the assemblies in the solid state.[1] Many of the new organic–inorganic hybrid materials with cavities or channels reported so far represent an illustrative example of the utilisation of such protocols.[2] Particularly, these hybrid materials are of great interest due to their structural diversity and their potential, among others, as porous solids. The concert of metals and organic components provides an augmented functionality to these hybrid solids in relation to the individual constituents.[2a,3a] For instance, metal centres are potential carriers of electrochemical, magnetic, catalytic, or optical properties that may be introduced into the organic–inorganic solid.[3] However, from a purely structural viewpoint, a metal centre also provides the ligand orienting ability of its well-known co-ordination environment to form inorganic hydrogen bonded assemblies[4] or co-ordination polymers.[5] Recently, these two approaches involving metal centres in extended molecular architectures have been combined to obtain a 1-D co-ordination polymer, which is assembled through self-complementary hydrogen bonds between correctly oriented pendant ligands.[2b] A third approach is that a metal may also be located in the supramolecular domain[6] (the periphery) of the metal–ligand building block. Thus, the metal would be exposed to the environment and could participate in directional intermolecular interactions, providing an additional tool to be used in the control of the final assembly. The focus to incorporate the metal in such intermolecular interactions has relied on the study of hydrogen bonds involving metal centres.[7a] In contrast, other directional interactions (typical examples are M···halide, M···O, and M···M) have been less considered in the crystal engineering context.[7b] In the present investigation, the synthesis of a highly pure phase mesoporous array of silver(I) and isonicotinic entities is described. The unusual supramolecular architecture is achieved by the concurrence of three different strategies to assemble a metal-based building block.

Experimental

All the reagents were commercially available and used as received from Aldrich. Elemental analyses (C, H, N) were performed on a model EA1108 Fisons elemental analyser. FTIR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Magna IR 560 spectrophotometer.

Surface area and porosity were measured with a Micromeritics ASAP 2010 apparatus. A full adsorption isotherm was obtained using N_2 as adsorbate (77 K). Data were processed to calculate porosity distribution and surface area by using density functional theory (DFT)[8a] and the Brunauer–Emmet–Teller (BET)[8b] method, respectively.

Thermal analysis was performed by using a Dupont Instruments 951 thermogravimetric analyser. Experimental conditions: 9.1 mg of sample, N_2 atmosphere, heating rate 10 °C min^{-1} and T_{max} 800 °C.

The powder X-ray diffraction pattern was recorded in a Siemens D5005 diffractometer with graphite-monochromated Cu-Kα radiation ($\lambda = 1.5406$ Å).

Synthesis of $\{[Ag(Iso)(HIso)]_{1/2} \cdot [Ag(Iso)]\}_n$

To a hot and stirred solution of isonicotinic acid (0.170 g, 1.38 mmol) in 20 ml of ethanol, a preheated solution of $AgBF_4$ (0.238 g, 1.44 mmol) in 5 ml of water was added dropwise. The flask was covered with aluminium foil and left to stand at room temperature. After 24 h a white solid together with transparent rod crystals had formed; these were filtered off and washed with hot ethanol. XRD experiments showed that the bulk represents the same phase as observed in the single crystal. IR (KBr, cm^{-1}): $\upsilon_{asym}(CO_2)$ 1543, 1606; $\upsilon_{sym}(CO_2)$ 1393, 1400; $\upsilon(OH)$ 3429. Anal. calc. for $C_{12}H_{8.5}N_2O_4Ag_{1.5}$: C, 35.94; H, 2.15; N, 6.77; found: C, 35.96; H, 1.93; N, 6.74%.

X-Ray crystallography

A single crystal determination was made on a Rigaku AFC7S diffractometer. Crystal data: Formula $C_{12}H_{8.5}N_2O_4Ag_{1.5}$,

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$M = 406.51$ g mol^{-1}, monoclinic, space group $P2_1/c$, $a = 8.157(4)$, $b = 19.586(11)$, $c = 7.404(2)$ Å, $\beta = 92.80(3)°$, $U = 1181.5(9)$ Å^3, $Z = 4$, μ(Mo-Kα) $= 2.523$ mm^{-1}, $T = 25$ °C, $\omega - 2\theta$ scan, semi-empirical absorption correction. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in their calculated positions in the last cycle of the refinement, except for H6 whose position was found on an inversion centre (1/2, 0, 0) between two oxygen atoms. The isotropic displacement parameter for H6 was refined freely. There were 2509 total reflections measured, of which 1204 unique reflections were used in the refinement. $R_1 = 0.0215$ and $wR_2 = 0.0527$.

CCDC reference number 154453. See http://www.rsc.org/suppdata/nj/b1/b106297m/ for crystallographic data in CIF or other electronic format.

Results and discussion

Formation and structure

The reaction of $AgBF_4$ with isonicotinic acid (HIso) in a 1 : 1 ratio leads to the formation of the silver(I) assembly. The solid product consists of two different 1-D extended arrangements; a hydrogen bonded assembly [Fig. 1(a)] and a co-ordination polymer [Fig. 1(b)]. The building blocks that form both 1-D assemblies are labelled in Fig. 1. In the first building block, silver(I) is co-ordinated to two isonicotinic moieties through the nitrogen atoms [*d*(Agl–N1): 2.151(3) Å]. The metallic ion lies on a centre of symmetry, leading to a linear N1–Ag1–N1A co-ordination geometry and, consequently, to a co-planarity between both pyridine rings. Each carboxylic acid group is nearly co-planar with the corresponding pyridine ring, resulting in a dihedral angle of 4.7°. This metallic building block is assembled in a linear 1-D arrangement [Fig. 1(a)] by charge-assisted carboxylate–carboxylic acid hydrogen bonds[9] (O···H···O). Thus, the shared hydrogen atom also lies on an inversion centre [*d*(O1···O1B): 2.474 Å]. Therefore, the carboxylic acid unit shows asymmetric C–O bond distances [*d*(C6–O1): 1.279(7) and *d*(C6–O2): 1.213(7) Å]. This building block can thus be formulated as a neutral [Ag(Iso)(HIso)] complex. It is noteworthy that such a building block and its 1-D arrangement have also been observed in the crystal structure of the complex $[Ag(Iso)(HIso)]\cdot 4H_2O$.[10] Analogously, Aakeröy *et al.*[11] reported a 2-D architecture sustained by a similar charge-assisted carboxylate–carboxylic acid hydrogen bond by using isonicotinic acid and the orienting ability of Pd(II) to form square planar arrangements.

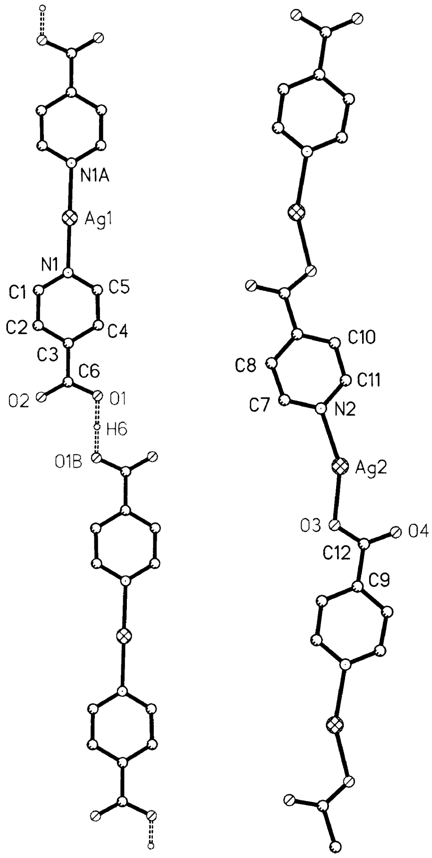

Fig. 1 Two different 1-D extended systems observed in the crystal structure of $\{[Ag(Iso)(HIso)]_{1/2}\cdot[Ag(Iso)]\}_n$. (a) The [Ag(Iso)(HIso)] linear building block is assembled *via* charge-assisted carboxylate–carboxylic acid hydrogen bonds. Labels containing A and B correspond to molecular fragments generated by centres of symmetry. (b) Representation of a strand of the $[Ag(Iso)]_n$ co-ordination polymer in which the metals are linked *via* coordinative bonds.

In the co-existing building block [Fig. 1(b)], each silver ion is co-ordinated to a pyridine nitrogen [*d*(Ag2–N2): 2.173(4) Å] and one oxygen atom of the carboxylate group [*d*(Ag2–O3): 2.133(3) Å], forming an N2–Ag2–O3 bond angle of 155.6(2)°. The monodentate carboxylate also shows asymmetric C–O bond distances [*d*(C12–O3): 1.269(8) and *d*(C12–O4): 1.228(7) Å]. Both heterocyclic rings are nearly co-planar and form a dihedral angle of 5.3° between them and 9.3° with the corresponding carboxylate group. In view of the deviation from linearity of the silver co-ordination geometry, the ligand spacer expands the metal centre to form a slightly wavy 1-D co-ordination polymer. This 1-D assembly can be formulated as a neutral $[Ag(Iso)]_n$ polymer. Unlike the [Ag(Iso)(HIso)] complex, a similar silver 1-D co-ordination polymer has not been reported. However, an 1-D polymeric species based on silver(I) triangles linked by isonicotinate anions was described by Burrows *et al.*[12] Recently, two co-ordination polymers involving isonicotinate as a spacer, to expand Cu(II)[13] (2-D polymer) and Fe(II)[14] (3-D polymer) metal ions, have also been reported.

In the crystal structure it is possible to observe families of hydrogen bonded assemblies running parallel to each other in the *ac* plane (Green strands in Fig. 2) sustained by π–π interactions, in which every pyridine ring is sandwiched between a carboxylate moiety (average: 4.0 Å) and another pyridine ring (average: 3.9 Å). The shortest Ag···Ag and Ag···O distances between neighbouring hydrogen bonded arrays (7.404 and 3.505 Å, respectively) preclude the existence any interaction between these atoms.[15] Furthermore, strands of the co-ordination polymer (magenta strands in Fig. 2) appear to run

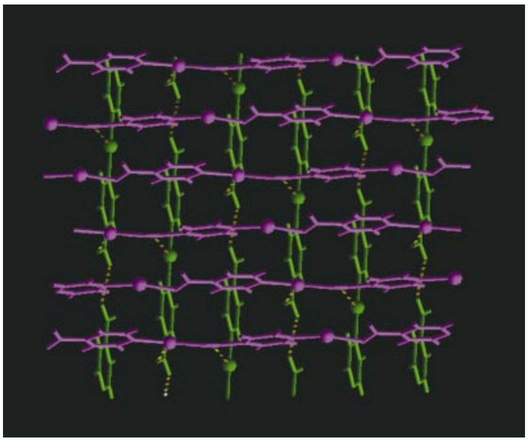

Fig. 2 View of the hydrogen bonded 1-D extended arrays of [Ag(Iso)(HIso)] (green) and of the $[Ag(Iso)]_n$ co-ordination polymers (magenta) depicting the plywood-like packing through Ag···O interactions.

parallel to each other, all being accommodated in the same plane, which in turn is also parallel to the plane formed by the family of hydrogen bonded assemblies. In the planes defined by the strands of the co-ordination polymer, π–π interactions between carboxylate groups (average: 4.1 Å) and face-to-face interactions between the heterocyclic rings (average: 3.8 Å) are observed. However, more striking is that besides the π–π interactions, additional Ag2···O3 (3.092 Å) intermolecular interactions also help to support the parallel arrangement of the co-ordination polymer. The shortest Ag···Ag distances (3.804 Å) between adjacent co-ordination polymer chains preclude any metal-metal interaction.[15a] Each plane containing the hydrogen bonded assemblies and the one defined by the co-ordination polymer chains are plywood-like,[16] packed in the *b* axis direction and linked together almost exclusively through Ag···O intermolecular interactions.[17] A silver ion of a hydrogen bonded assembly participates in inter-chain Ag1···O4 (2.852 Å) interactions with an uncoordinated oxygen atom of an adjacent co-ordination polymer chain. Similarly, every strand of the co-ordination polymer exposes its metal centres to form a shorter Ag2···O2 inter-chain bond (2.661 Å) with the oxygen of the hydrogen bonded extended arrays. This short distance suggests a strong Ag···O interaction, which could be responsible for the deviation from linearity observed in the metallic geometry of the co-ordination polymer. The molecular axes of every hydrogen bonded 1-D array and those of the co-ordination polymers are at 92.8° (see Fig. 2) corresponding to the β angle, although both directions are found to be slightly rotated with respect to those of the *a* and *c* axes.

Size pore distribution and thermal analysis

At a first glance, the view shown in Fig. 2 resembles a square grid with cavities of up to ~4 × ~4 Å. Therefore, the plywood arrangement allows the cavities to be interconnected to form continuous channels in the 3-D structure. This unique assembly prompted us to examine the porosity by mean of the N_2 adsorption method. Fig. 3 shows the typical pore size distribution obtained using the DFT method, which indicates that no micropores are present in the material. In contrast, this distribution lies almost exclusively inside of the range corresponding to mesoporous materials (20–500 Å) with a maximum at ~30 Å. On the other hand, the BET total surface area measurement shows a value of 242 $m^2\ g^{-1}$.

The TG curve shows three steps between 210–530 °C with a total weight loss of 58.8% attributed to the decomposition of the organic ligand (~61% calc.). The initial step (210–270 °C) is accompanied by ~15% mass loss and could be associated with decarboxylation of 1.5 mol (~16.2% calc.) of CO_2. The second and third weight loss (270–530 °C) be attributed to the last steps of decomposition of the organic moiety, accompanied by reduction of silver oxide to yield Ag metal. Precisely, the resulting mass of the final product (~41.2%) between 530–800 °C was attributed to Ag metal (~39.8% calc.). C, H, N or S elements were not found in this final product as determined by elemental analysis. The formation of both CO_2 and Ag metal products has already been suggested for the decomposition of silver maleate and silver fumarate.[18]

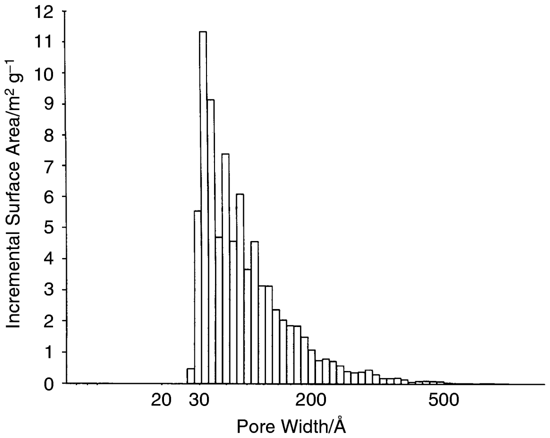

Fig. 3 Pore size distribution for $\{[Ag(Iso)(HIso)]_{1/2}\cdot[Ag(Iso)]\}_n$ obtained using the DFT method.

In summary, it has been possible to synthesise an unusual mesoporous silver(I) solid built from two structurally different 1-D metal-based assemblies. Both extended arrays are held together by π–π interactions between isonicotinic moieties and by using intermolecular interactions of the type Ag···O. This crystal structure is an illustrative example of the concurrence of different metal-based assemblies to achieve a new supramolecular architecture.

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