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Design of novel 2D porous coordination polymers based on metallacrown units

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Abstract: A 12-metallacrown-4 (MC) complex was designed and employed as the building block in the synthesis of coordination polymers, one of which is the first permanently porous MC architecture. The connection of the four-fold symmetric MC subunits via Cu^{II} nodes led to the formation of 2D layers of metallacrowns. Channels are present in the crystalline architecture, which exhibits permanent porosity manifested in N₂ and CO₂ uptake capacity.

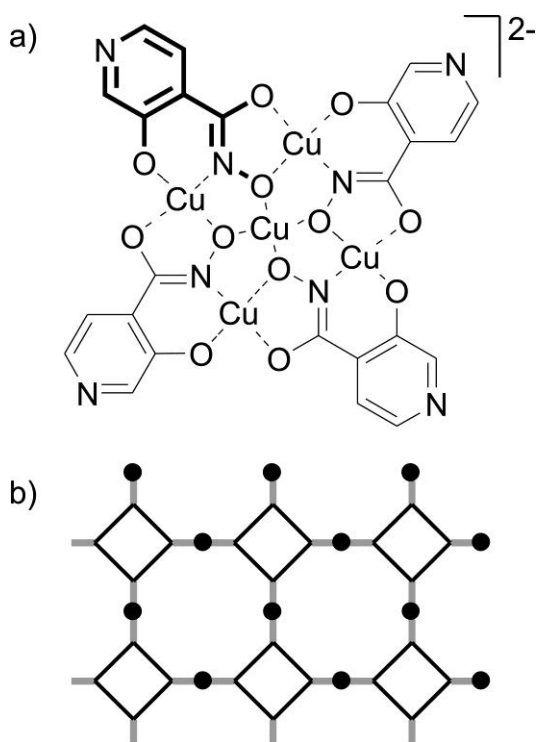
Main text

The chemistry of porous coordination polymers (PCPs) is a subject of extensive investigation due to its interesting applications in gas adsorption and purification, catalysis, luminescence and magnetism.^[1] The use of metal-rich entities as building blocks in the assembly of PCPs has allowed for the preparation of materials with functional properties that are derived from the individual molecular units (*e.g.* luminescence or slow magnetic relaxation).^[2]

Metallacrowns (MCs, Scheme 1a) are self-assembled metallamacrocycles that can be described as inorganic analogues of crown ethers, where the C-C bonds are replaced by metal-heteroatom bonds.^[3,4] Both classes of compounds have central cavities which can coordinate metal ions ranging in size from transition and main group metals, to larger lanthanide ions.^[3,4] MCs are promising precursors to advanced materials and probes that utilize the electronic, optical and magnetic properties derived from the confinement of several metal ions within a molecular framework of small dimensions.^[4,5] For instance, MCs containing NIR-emitting lanthanides have been shown to display outstanding quantum yields and lifetimes, opening up the possibility for applications such as *in-vivo*

imaging.^[6] Additionally, in the field of magnetism, several MCs have been reported to exhibit single-molecule magnet behavior.^[4,5] With this in mind, we were attracted by the possibility of combining the versatile properties of MC scaffolds together with the permanent porosity of PCPs. The resulting hybrid solids may have interesting properties, suitable for applications ranging from the field of guest-responsive luminescent sensors, to the field of advanced magnetic materials.

MCs are solution stable in a wide range of conditions^[3,7] and can be easily isolated in the solid state. Nevertheless, only a few examples of extended frameworks^[8-10] or supramolecular architectures^[11-13] composed of MC units have been reported to date. Furthermore, none of these compounds display the permanent porosity that is typical of porous coordination polymers. One reason for the lack of porosity is the fact that MCs are often linked through ditopic bridging ligands (*e.g.* dicarboxylates), which coordinate to the axial positions of the metal ions in the MC framework.^[9,11,14] This type of connection favors the formation of chains of MCs, which tend to crystallize in close proximity to each other, therefore reducing the void space necessary for significant porosity.



Scheme 1. a) Scheme of $\{\text{Cu}^{\text{II}}[12\text{-MC}_{\text{CuII, hinHA}^3}\text{-4}]\}^{2-}$. The ligand hinHA^{3-} is highlighted; b) Schematic representation of the 2D layers of metallacrowns.

Two examples of multidimensional coordination polymers formed by the linkage of MCs through functional moieties placed on the periphery of the molecular framework have been reported.^[8] However, permanent porosity was not observed for either one of the lattices.^[8] Furthermore, there are a few examples void-space containing networks formed by the aggregation of MCs held together by weak interactions.^[12,13] As with the first example, the interactions established in these architectures do

not provide sufficient structural stabilization for the lattices to exhibit significant gas uptake properties. Also, these (pseudo)-porous extended frameworks were formed by serendipitous spatial arrangement of the MC units, rather than from the rational design and control of the interactions established between the building blocks.

In this paper we present two novel MC networks, one of which is the first permanent PCP made of metallocrowns that is resistant to solvent evacuation and capable of adsorbing gas. In this architecture, 12-MC-4 units were assembled using Cu^{II} ions and a pyridinic analogue of salicylhydroxamic acid as ligand (hinHA^{3-} , Scheme 1a). We aimed to connect these MC units through in-plane metal ion bridges to form a chessboard-like fourfold arrangement (Scheme 1b). Hence, the ligand was designed to provide the MC with pyridine-like moieties pointing towards the exterior of the scaffold, in order to increase the propensity for forming peripheral coordination bonds. These bonds were designed to impose proper distance between MC units in order to generate voids within the lattice.^[8a]

The ligand H_3hinHA (3-hydroxyisonicotine hydroxamic acid) was synthesized in moderate yield from the carboxylic acid precursor using activation-deprotection strategies.^[15] The reaction of Cu^{II} salts with H_3hinHA selectively provided a $\{\text{Cu}^{\text{II}}[12\text{-MC}_{\text{CuII, hinHA-4}}]\}^{2-}$ species, as observed by mass spectrometry (ESI-MS, Figure S8, Supporting Information). By modifying reaction conditions, we were able to isolate two distinct MC networks.

Network **1** (Figure 1) was isolated by reacting H_3hinHA with Cu^{II} acetate in a 1:1.75 ratio in a dilute 2:1 DMF:Pyridine solution, followed by slow evaporation of the solvent. The structure is composed of stacked two-dimensional coordination networks with the formula $\{[\text{Cu}^{\text{II}}(\text{AcO})\text{Py}]_2\{\text{Cu}^{\text{II}}[12\text{-MC}_{\text{CuII, hinHA-4}}]\}\}_n$. As shown in Figure 1, single units of the $\{\text{Cu}^{\text{II}}[12\text{-MC}_{\text{CuII, hinHA-4}}]\}^{2-}$ metallocrown are bridged by additional Cu^{II} ions coordinated to the peripheral pyridinic moieties of two neighboring MC units. The bridging Cu^{II} nodes have the formula $[\text{Cu}^{\text{II}}(\text{AcO})\text{Py}]^+$: their coordination geometry can be described as distorted square planar, where the two MC pyridinic moieties coordinate to the linking metals in a *trans* fashion. The remaining positions are occupied by a monodentate acetate ion and a solvent pyridine molecule (Figure 1b). The result is the formation of a chessboard-like arrangement of 12-MC-4 units, in which the voids have a rectangular shape. Interestingly, each layer is not planar, but rather has a wave-like topology, as the result of the bowl-shaped MC units.

In the MC unit, each of the five Cu^{II} ions is coordinated axially by one solvent molecule of pyridine, and exhibits a distorted square pyramidal coordination geometry (Figure S14, Supporting Information). Due to steric interactions, the four ring ions are all coordinated by the pyridine molecules on the MC convex face, while the central Cu^{II} ion is coordinated by the fifth pyridine on the opposite face (Figure 1b).

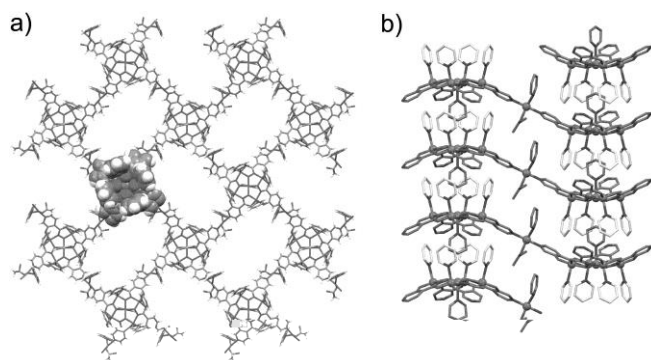


Figure 1. a) Representation of one layer of the porous network **1**, viewed along the c axis. One MC unit is shown in a space filling representation. Taking into consideration Van der Waals radii, the 2D pore section measures $12.6 \times 8.9 \text{ \AA}^2$, accounting for 36% of the total cell volume. b) Encapsulation of a coordinated pyridine molecule within the hydrophobic pyridinic pocket forms π - π pillars holding the layers together.

One structural consequence of this pyridine distribution is the disruption of planarity leading to the bowl shape of the MC units. In this non-planar configuration, the prochiral MC units gain chirality, as one can distinguish the clockwise or anticlockwise rotation of the $(\text{Cu-O-N})_4$ cyclic repetition of the MC ring, with respect to the concave face of the molecule (Figure S12, Supplementary Information).^[16] Since the crystal lattice is formed by the wave-like repetition of only one of the two possible enantiomers, a homochiral coordination polymer which crystallizes in the chiral space group $P42_12$ is obtained.

The four pyridine molecules coordinated to the same face of an MC subunit forms an aromatic pocket that encapsulates the lone pyridine of the neighboring 2D layer (Figure 1b). This columnar stacking of interpenetrated pyridines creates π - π pillars, which provide stability to the assembly and allow the rectangular void spaces of each layer to be perfectly stacked, one above the other, to form void channels that run along the entire crystal (Figure 2). Since the charge balance is provided by the bridging $[\text{Cu}^{\text{II}}(\text{AcO})\text{Py}]^+$ units, no extra counter ions, which may potentially occupy the void spaces, are required. By taking into consideration the Van der Waals radii, the estimated channel cross section measures $12.6 \times 8.9 \text{ \AA}^2$ and accounts for 36% of the total unit cell volume, as estimated by PLATON.^[17] The channels are filled by disordered solvent molecules, which can be removed by thermal treatment of the solid at moderate temperatures, without loss of crystallinity (see below).

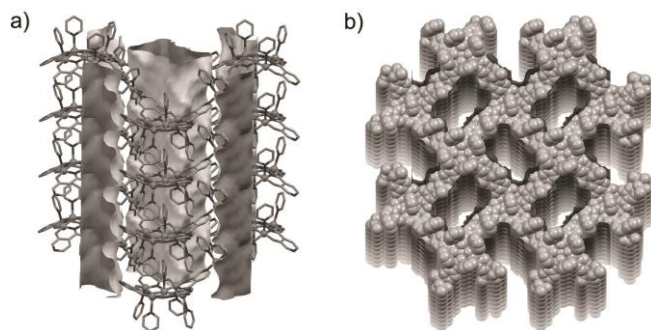


Figure 2. a) Side view of the void channels formed by the vertical stacking of MC layers. The MC network is represented as sticks; the channels were generated by rolling a spherical probe of radius 1.2 Å on the surface of the voids. b) Top-down view of the rectangular-shaped channels running along the crystal; the atoms of the network are shown as spheres.

The thermal stability of the crystalline network **1** was investigated through thermogravimetric analysis (TGA) and variable-temperature powder x-ray diffraction (PXRD, Figure 3) on a solvent-exchanged batch of crystals (CH_2Cl_2 , three times over three days). The TGA curve displayed a sharp weight loss of 15% between 50-65 °C, corresponding to the loss of adsorbed solvent in the void channels (Figure 3a). The plateau between 65-320 °C suggests that the network is thermally stable over this temperature range; at higher temperatures, decomposition of the organic matrix takes place. No loss of crystallinity is observed below 225 °C, as shown in the PXRD patterns in Figure 3b. These results suggest high thermal resistance of the crystal lattice to degradation.

The porosity of compound **1** was studied by isothermal nitrogen adsorption at 77 K on crystals activated by solvent exchange followed by heating at 110 °C under vacuum for 6 hours. The surface area was determined to be $515 \text{ m}^2 \text{ g}^{-1}$ and $568 \text{ m}^2 \text{ g}^{-1}$ according to the BET and Langmuir methods respectively, with a total pore volume of $0.583 \text{ cm}^3 \text{ g}^{-1}$. The activated network was also tested for isothermal CO_2 adsorption up to 1 atm at 195 K and at 273 K, exhibiting CO_2 uptake capacities of 23.3 wt% ($118.64 \text{ cm}^3 \text{ g}^{-1}$, 5.31 mmol g^{-1}) and of 7.3 wt% ($37.27 \text{ cm}^3 \text{ g}^{-1}$, 1.66 mmol g^{-1}), respectively.^[18] These values are comparable to the CO_2 adsorption capacities of other reported porous MOFs.^[19] For both N_2 and CO_2 , the isotherms show a type-I behavior at lower gas pressures (Figure 3);^[20] such behavior is in agreement with the microporous nature of the solid, as indicated by the crystal structure. Hence, we can conclude that network **1** is the first permanently porous coordination polymer made of MCs and is capable of reversible gas adsorption.

Figure 3. a) Thermogravimetric analysis of solid **1**, run under a N₂ atmosphere up to 600 °C; b) Variable-temperature powder-XRD spectra of **1** in the 25-305 °C interval; c), d) Isothermal gas adsorption of **1**, respectively N₂ at 77 K and CO₂ at 195 K and 273 K.

A detailed description of the coordination polymers based on metallocrowns has been reported recently.^[21] Compared to the compounds known to date, network **1**, with its average calculated pore diameter of 1.2 nm and 36% of total void volume, possesses the second widest pores of all MC-based systems, behind the mesoporous aggregate La^{III}/Cu^{II} 15-MC-5 (average pore diameter of 2.4 nm with 43% of unit cell voids).^[12] However, the aforementioned mesoporous material does not withstand solvent evacuation and, therefore, does not show permanent porosity due to structural collapse upon solvent removal. A few other MC-based supramolecular assemblies have exhibited good uptake capacities towards alcohols,^[13] though these sorption properties are not caused by the presence of porous lattices, but rather by compact, non-porous structures undergoing uptake mechanisms known as “gate-opening”.^[13,21] On the other hand, compound **1** is a coordination polymer characterized by wide structured pores and by a crystal lattice resistant to solvent evacuation, attributes that effectively classify the framework as a porous material.

Reacting H₃hinHA, Cu^{II} triflate and tetraethylammonium (NEt₄⁺) acetate (1:1.25:3 ratio) in a solution of 3:2:1 DMSO:DMF:pyridine led to the isolation of a different network (**2**), which has the formula {(NEt₄)₂{Cu^{II}[12-MC_{CuII, hinHA}-4]}(DMSO)₂}_n.^[22] Single-crystal X-

other. The four ring Cu^{II} ions exhibit a square pyramidal coordination geometry, where the axial positions are occupied alternately either by a nearby MC pyridinic moiety or by a DMSO molecule (Figure 4a). The charge of each MC unit is balanced with two bulky NEt_4^+ ions occupying the rectangular interstices created between the linked MCs, leading to a non-porous solid (Figure 4b). The isolation of **2** in place of **1** is likely due Cu^{II} :ligand 5:4 stoichiometric ratio required to assemble the MC units, leaving no extra metal ions available to act as the linkers. However, the coordinated DMSO also plays a role, as it prevents the formation of the pyridine aromatic pockets required to stabilize the interactions between layers in **1**, thus favouring the crystallization of **2**. Interestingly, the MC units in **2** arrange into layers: single 2D reticular frameworks, parallel to the *bc* crystallographic plane, are held together by weak interactions between NEt_4^+ ions and the aromatic residues of adjacent MCs (Figure S13, Supporting Information).

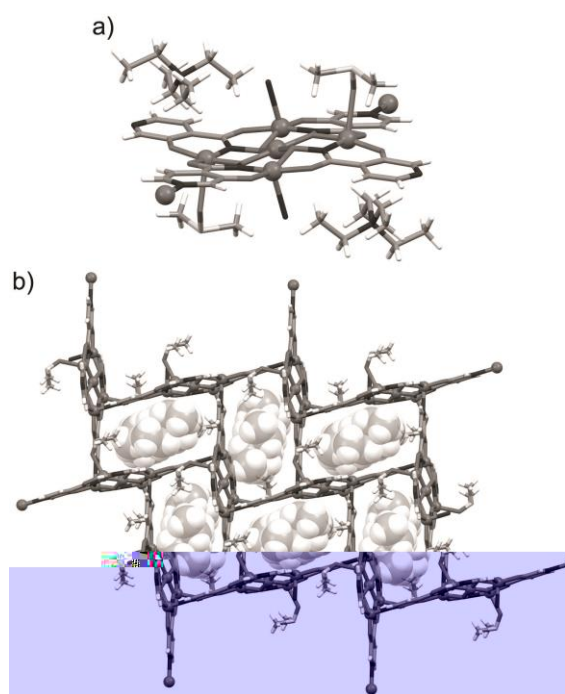


Figure 4. Structure of **2**, viewed along *a*. a) Single MC unit, with two coordinated DMSO molecules and two tetraethylammonium counter-ions; b) 2D-network established by cross-coordinated MC units, encapsulating tetraethylammonium (spacefill representation) in the interstices.

A 1D coordination polymer of 15-MC-5 made of pyrazinohydroxamic acid, a close analog of H_3hinHA , was previously reported in the literature.^[11] The connectivity between MCs was achieved by coordination of a peripheral pyridinic nitrogen onto a Cu^{II} ring ion of a nearby MC. However, neither 2D nor 3D assemblies were generated, possibly due to the five-fold symmetry of 15-MC-5, which complicates the establishment of such frameworks.

Here, the ability of hinHA^{3-} to assemble into stable, four-fold symmetric 12-MC-4 units and to provide donor atoms for the linkage of MC units through the coordination of bridging metal ions is

fully exploited in **1**. Network **2**, although not porous, further demonstrates the tendency of 12-MC-4 of hinHA³⁻ to form coordination polymers and opens the possibility for synthesizing other novel materials using this ligand and different metals.

In conclusion, the newly designed H₃hinHA proved to be a versatile and reliable organic ligand for the production of extended networks. With the design and isolation of network **1**, we succeeded in obtaining the first homochiral MC-based permanently porous coordination polymer which exhibits good gas adsorption capacity. This network represents a proof-of-concept of how the rational design of MC units may lead the way for a new class of functional porous materials based on high interest MC synthons. We now aim at exploiting the porosity of new MC-based frameworks to realize functional guest-responsive devices, with applications ranging from luminescent sensors to advanced magnetic materials, to catalysis.

Acknowledgements

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Scheme and figure legends

Scheme 1. a) Scheme of $\{\text{Cu}^{\text{II}}[12\text{-MC}_{\text{CuII,hinHA-4}}]\}^{2-}$. The ligand hinHA^{3-} is highlighted; b) Schematic representation of the 2D layers of metallacrowns.

Figure 1. a) Representation of one layer of the porous network, viewed along the *c* axis. One MC unit is shown in a space filling representation. Taking into consideration Van der Waals radii, the 2D pore section measures $12.6 \times 8.9 \text{ \AA}^2$, accounting for 36% of the total cell volume. b) Encapsulation of a coordinated pyridine molecule within the hydrophobic pyridinic pocket forms π - π pillars holding the layers together.

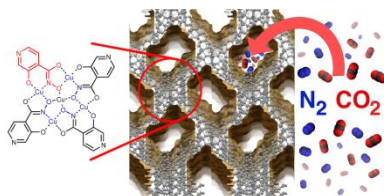
Figure 2. a) Side view of the void channels formed by the vertical stacking of MC layers. The MC network is represented as sticks; the channels were generated by rolling a spherical probe of radius 1.2 \AA on the surface of the voids. b) Top-down view of the rectangular-shaped channels running along the crystal; the atoms of the network are shown as spheres.

Figure 3. a) Thermogravimetric analysis of solid **1**, run under a N_2 atmosphere up to 600 $^\circ\text{C}$; b) Variable-temperature powder-XRD spectra of **1** in the 25-305 $^\circ\text{C}$ interval; c), d) Isothermal gas adsorption of **1**, respectively N_2 at 77 K and CO_2 at 195 K and 273 K.

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Table of Contents

Permanently porous metallacrowns: Metallacrowns have been exploited for the first time as tailored building blocks for the achievement of new (porous) coordination polymers. Metallacrowns are metal-rich complexes that have exhibited excellent properties in magnetism and luminescence. Benefiting from high-interest metallacrown building blocks in the synthesis of MOFs can unfold a whole new class of functional materials.



Keywords:

Metallacrowns • Coordination polymers • Gas adsorption • Hydroxamic acids • Porosity