Control of coordination chemistry in both the framework and the pore channels of mesoporous hybrid materials†

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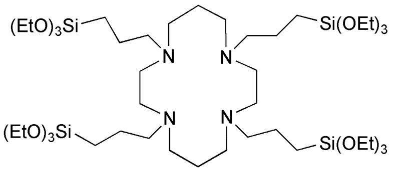
Mesoporous materials containing bridged cyclam moieties inside the framework were prepared by using a neutral templating route. Quantitative formation of bridged Cu^{II}-cyclam complexes was obtained by the direct incorporation of CuCl$_2$ inside the hybrid material, showing thus the complete accessibility of cyclam moieties located inside the framework. Grafting of a metal-*N*-triethoxysilylpropylcyclam complex inside the channel pores followed by the incorporation of another metal salt into the framework gave rise to an hybrid material containing two strongly chelated metal salts, one located inside the framework, the other in the channel pores.



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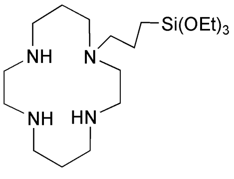

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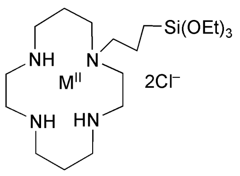

M = Cu 3Cu
M = Co 3Co

The development of nanomaterials (*i.e.*, materials prepared from molecular precursors) is one of the important stakes in the field of chemistry. With this view, to find methods allowing the selective introduction of transition metal or lanthanide ions into appropriate materials is essential as these ions exhibit important physical properties (optic, magnetic, *etc.*). For this purpose, mesoporous systems and more specifically mesoporous hybrid materials of the polyoxometallate (POM) type[1–6] (materials in which the organic fragments are distributed within the framework and covalently linked to the silica matrix) are particularly interesting in that they open the possibility to couple two physical properties, one in the framework and another in the pore channels,[7–9] *via* the selective introduction of transition metal or lanthanide ions. In this paper, we show for the first time that it is possible to specifically introduce, by using chelating cyclam units covalently linked to the silica matrix,[10] one metal cation (Cu^{II}) in the pore channels and another (Co^{II}) in the framework (and the reverse), proving thus the complete control of the coordination chemistry in these materials. The method is general and was even extended to lanthanide ions located in the framework with Cu^{II} in the channel pores.

Co-hydrolysis and polycondensation of the tetra-*N*-silylated cyclam derivative **1**[11] (cyclam is the 1,4,8,11-tetraazacyclotetradecane well-known for its remarkable binding ability towards transition metals salts[12,13]) with 9 molar equivalents of TEOS in the presence of tergitol 15-S-12, [C$_{15}$H$_{31}$O(CH$_2$CH$_2$O)$_{12}$H],[14–16] as a surfactant template gave rise, under neutral conditions, to the mesoporous hybrid material **2**,[10] the textural data of which are given in Table 1. The N$_2$ adsorption-desorption isotherm of material **2** is reported in Fig. 1. ^{13}C solid-state cross-polarization magic angle spinning NMR spectroscopy (CP-MAS) indicated that the cyclam groups survive the hydrolytic polycondensation and are intact inside the channel walls. The composition of **2** was inferred from the results of elemental analysis of nitrogen and silicon. It was found to be close to that for the original mixture (Table 1). A SAXS analysis of **2** revealed the absence of a Bragg peak. However, the diffractogram presents a linear part of q^{-1} slope, characteristic of non-correlated channels[17] (see Electronic supplementary information, ESI).

Complexation of Cu^{II} by the cyclam moieties incorporated inside the framework was subsequently achieved by treatment of **2** with an ethanol solution containing 1.4 equiv. of CuCl$_2$. After heating under reflux for 24 h, the resulting solid **2**Cu was filtrated off and copiously washed with ethanol. Conductimetric titration of the whole filtrate containing the uncomplexed salt was done and revealed the incorporation of one Cu^{II} per cyclam unit. This result was confirmed by the elemental analysis of **2**Cu (Table 1). Thus, all the cyclam moieties are accessible due to the diffusion of the ethanolic solution of the transition metal salt through the walls. Incorporation in the framework of Eu^{III}, which is a luminescent centre, and Gd^{III}, known for is magnetic properties, was also investigated. This was achieved by treatment of **2** with an ethanol solution heated under reflux for 24 h and containing 2 equiv. of lanthanide salt (Table 2). Complexometric titration of the excess of lanthanide salt as well as elemental analysis of the resulting materials **2**Eu and **2**Gd revealed the incorporation of one Ln^{III} *per* 2 cyclam moieties. These results are in agreement with those obtained from the materials prepared by hydrolysis and polycondensation of **1**[18] in the absence of surfactant: direct incorporation of Cu^{II} into these materials led to the formation of 1:1

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† Electronic supplementary information (ESI) available: SAXS pattern of material **2**. See http://www.rsc.org/suppdata/nj/b3/b302027d/

Table 1 Some relevant characteristics of different mesoporous hybrid materials

Entry	Sample	S_{BET}/m^2 g^{-1}	V_p/cm^3 g^{-1}	$D_p{}^a$/Å	**3**:**1**:SiO$_2{}^b$	[**1**]^c/mmol g^{-1}	[**3**]^c/mmol g^{-1}	[Cu]^c/mmol g^{-1}	[Co]^c/mmol g^{-1}
1	**2**	703	1.46	87	0:1:9	0.80	0	0	0
2	**2**Cu	684	1.42	86	0:1:9	0.71	0	0.71 (0.74)	0
3	**2**–**3**Cu	250	0.61	72	0.7:1:9	0.59	0.38	0.40	0
4	**2**–**3**Co	221	0.49	61	0.8:1:9	0.57	0.35	0	0.41
5	**2**Cu–**3**Cu	307	0.62	61	1.45:1:9	0.37	0.54	0.90	0
6	**2**Co–**3**Cu	168	0.43	71	0.7:1:9	0.49	0.37	0.37	0.50 (0.49)
7	**2**Cu–**3**Co	204	0.45	58	0.8:1:9	0.47	0.33	0.51 (0.53)	0.34

[a] Calculated from the desorption branch by using the BJH method. [b] Molar ratio determined from elemental analysis between the cyclam moieties in the channel pores (noted as **3**), the cyclam moities inside the framework (noted **1**) and the silica. [c] Values determinated from elemental analysis; in parentheses are the values determinated by titration of the uncomplexed salt by conductimetric measurements.

cyclam-Cu^{II} complexes. Interestingly, evidence for Cu–Cu interactions in these materials was given by ESR spectroscopy.[19] As such interactions had been observed from the solution ESR spectra of dinuclear Cu^{II} complexes in which two cyclams rings are in a face-to-face conformation,[20] it was suggested that in the solid, the cyclam units are in close proximity to each other. The subsequent incorporation of Eu^{III} in this same material, in the place of Cu^{II} gave rise to 2:1 cyclam-Eu^{III} complexes. This is a confirmation of the proximity of the cyclam units, allowing thus the formation of the Eu^{III} complexes between two cyclam units.

Let us now consider the grafting of metal cyclam complexes inside the channel pores of **2**. For this purpose, the complexes **3**Cu and **3**Co were first quantitatively prepared by reaction of *N*-triethoxysilylpropylcyclam **3**[21] with a stoichiometric amount of CuCl$_2$ or CoCl$_2$ in ethanol. Grafting of the isolated complexes **3**Cu or **3**Co inside the channel pores of the material **2** was achieved by treatment of **2** with a toluene solution of **3**Cu or **3**Co, giving rise respectively to the materials **2**–**3**Cu (Scheme 1) and **2**–**3**Co. Some relevant characteristics of these materials are given in Table 1. **2**–**3**Cu was then subsequently treated with an ethanol solution containing an excess of CuCl$_2$, 24 h under reflux, to afford the material **2**Cu–**3**Cu (Scheme 1 and entry 5 in Table 1). Titration of the excess of CuCl$_2$ in the filtrate as well as the results of elemental analysis of **2**Cu–**3**Cu revealed the incorporation of one Cu^{II} *per* cyclam moiety in the whole material. Another way to obtain **2**Cu–**3**Cu consisted of grafting **3**Cu directly to **2**Cu. In contrast, grafting of metal-free **3**, which is in large excess, on **2**Cu led to a partial decomplexation of the framework during the grafting, as proven by the colouration of the filtrate and the elemental analyses (N, Si, Cu) of the resulting material. This behaviour is due to the better complexing power of the monosubstituted cyclam moieties in comparison to the tetrasubstituted one. This unsuccessful experiment shows the importance of the order of introduction of complexes and the complexation reactions in the material to avoid the displacement of metal ions.

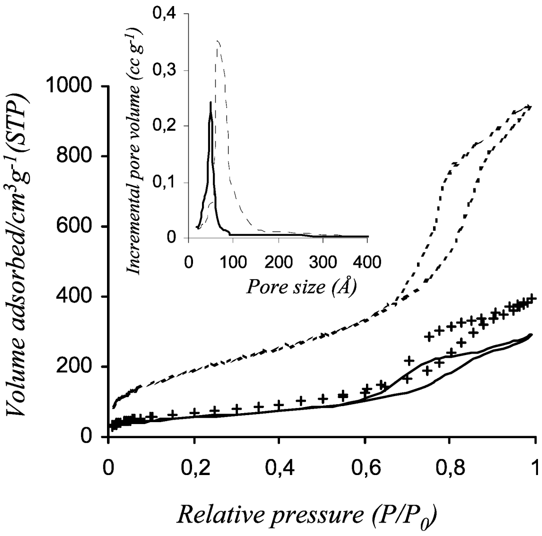


Fig. 1 Nitrogen adsorption-desorption isotherms and pore size distribution plot (inset) of **2** (---), **2**–**3**Cu (+) and **2**Co–**3**Cu (–).

We then attempted to introduce specifically one metal cation in the channel pores and another one in the framework. For this purpose, complexation of CoCl$_2$ by the cyclam moieties incorporated inside the framework of the material **2**–**3**Cu was carried out (Scheme 2) by treatment of **2**–**3**Cu with an ethanol solution containing 1.4 equiv. of CoCl$_2$ *per* cyclam moiety located inside the framework, giving rise to **2**Co–**3**Cu. Conductimetric titration of the filtrate revealed the incorporation of one Co^{II} *per* cyclam moiety. Quantitative formation of a Co^{II}-cyclam complex inside the framework was corroborated by the result of the elemental analysis of **2**Co–**3**Cu (Table 1, entry 6). As both methods of titration indicate the exact incorporation of one Co^{II} per cyclam moiety located inside the framework and not an excess, this demonstrates that there is no displacement of Cu^{II} by Co^{II}. A similar result was obtained by treatment of **2**–**3**Co with a solution containing 1.4 equiv. of CuCl$_2$ (Scheme 2), giving rise to the quantitative formation of **2**Cu–**3**Co (Table 1, entry 7).

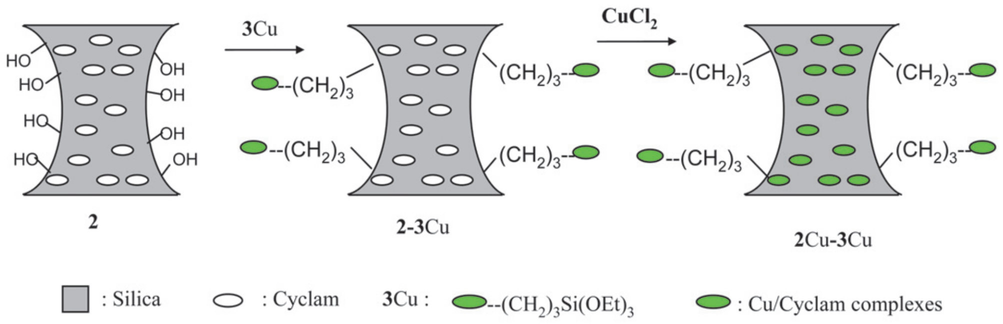
It is worth noting that in the materials **2**Co–**3**Cu and **2**Cu–**3**Co, the metal cation concentration in the pores is very similar in both cases (respectively 0.37 and 0.34 mmol g^{-1}). The same is true for the metal cation concentration in the framework of the same materials (0.51 and 0.50 mmol g^{-1}, Table 1).

The N$_2$ adsorption-desorption isotherm of **2**Co–**3**Cu is given as an example in Fig. 1. It reveals that the mesoporosity of the material is maintained. It is worth noting that grafting the complexes **3**Cu and **3**Co inside the pore channels of **2** produces in both cases a significant decrease of the BET specific areas, total pore volume (V_p) and mean pore diameters (D_p) as expected[22] (compare entries 1 and 3 and 1 and 4 in Table 1, Fig. 1). In contrast, complexation of metal ions by the cyclam moieties located inside the framework does not involve significant textural modifications (compare entries 1 and 2, 4 and 7 in Table 1). This is a further proof of the location of the cyclam moieties inside the framework.

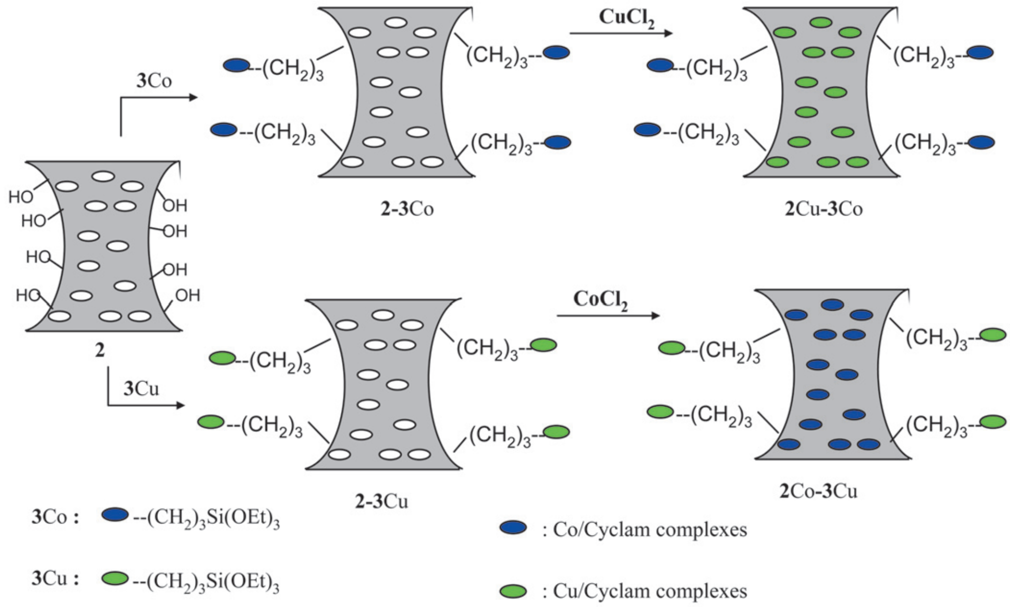
Table 2 Some relevant characteristics of mesoporous hybrid materials **2**Eu and **2**Gd

Sample	S_{BET}/m^2 g^{-1}	V_p/cm^3 g^{-1}	$D_p{}^a$/Å	[Ln]^b/mmol g^{-1}
2Eu	700	1.43	87	0.43 (0.41)
2Gd	687	1.40	86	0.37

[a] Calculated from the desorption branch by using the BJH method. [b] Values determinated from elemental analysis; in parenthese are the, values determinated by titration.



Scheme 1 Grafting of copper complex of *N*-triethoxysilylpropylcyclam **3**Cu on **2** followed by the incorporation of $CuCl_2$ into the framework, giving rise to **2**Cu–**3**Cu.



Scheme 2 Grafting of the cobalt complex **3**Co on **2**, followed by the incorporation of $CuCl_2$ into the framework, giving rise to **2**Cu–**3**Co (top). Grafting of the copper complex **3**Cu on **2**, followed by the incorporation of $CoCl_2$ into the framework, giving rise to **2**Co–**3**Cu (bottom).

Finally, grafting of **3**Cu inside the pore channels of **2**Eu gives rise to the material **2**Eu–**3**Cu containing 0.47 mmol g^{-1} of Cu and 0.30 mmol g^{-1} of Eu^{III}, showing thus the extent and the various possibilities of this methodology.

In summary, we have described the preparation of mesoporous hybrid materials containing two strongly chelated metal ions, one in the framework and the other in the pore channels, without displacement of one by the other. This was possible due to the difference of chelating power between *N*-tetrasubstituted cyclam moieties and the *N*-monosubstituted one. Such materials, able to couple two different physical properties such as magnetism and photoluminescence, for example, could open the way to smart materials.

Experimental

Preparation of material containing chelated Co(II) in the framework and chelated Cu(II) in the pore channels

2–**3**Cu was prepared by addition of **2** (270 mg, 0.24 mmol) to a solution of **3**Cu (850 mg, 1.57 mmol) in toluene (50 mL). The mixture was refluxed with stirring for 3 days. After filtration, the solid was washed several times with EtOH, and then dried at room temperature under vacuum to give 350 mg of **2**–**3**Cu. The incorporation of $CoCl_2$ inside the framework of **2**–**3**Cu was carried out by addition of **2**–**3**Cu (200 mg, 0.13 mmol) to a solution of $CoCl_2$ (24 mg, 0.18 mmol) in EtOH (30 mL). The mixture was refluxed and stirred for 24 h. After filtration, the solid was washed several times with EtOH, and then dried at room temperature under vacuum to give 190 mg of **2**Co–**3**Cu.

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