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Direct Synthesis of Functionalized Mesoporous Silica by Non-Ionic Assembly Routes. Quantitative Chemical Transformations within the Materials Leading to Strongly Chelated Transition Metal Ions

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This paper describes a general way permitting the quantitative introduction of strongly chelated transition metal ions. For that purpose, the direct synthesis of mesoporous silica containing chloropropyl groups has been achieved by using three different nonionic surfactants (*n*-hexadecylamine, tergitol 15-S-12, and the triblock copolymer P123) as structure-directing agents. Substitution of chloropropyl groups located within the pores by cyclam was then investigated; cyclam (1,4,8,11-tetraazacyclotetradecane) is well-known for its remarkable binding ability toward transition metal salts. We showed that the substitution of chloro groups by the cyclam depends on the mean pore size of the material. Anchoring of the cyclam moieties occurred almost quantitatively within the materials prepared in the presence of the triblock copolymer P123 and that without modification of the mesostructure. The binding ability of the cyclam toward transition metals salts was tested with $CoCl_2$ and $CuCl_2$. It was found to be maintained within the materials. All the cyclam moieties located within the pores' channels are accessible, leading to materials containing strongly chelated transition metal ions.

Introduction

The use of surfactant as a structure-directing agent for the synthesis of mesostructured silica has constituted a major discovery in the material science in the past decade.[1−6] These materials are characterized by high surface areas, uniform and controlled pores sizes, and long-range order. They have attracted the attention of numerous scientists, who studied the functionalization of their surface in order to render them suitable for practical applications such as catalysis, ion exchange, and optical or magnetic properties. For that purpose, postsynthesis grafting of an organotrialkoxysilane $RSi(OR')_3$ via SiOH groups of hexagonally ordered MCM-41 was very often used because of its high surface area and uniform pore-size distribution.[7−11] This method is general and allows the grafting of even bulky organic groups by choosing a mesoporous silica with a convenient pore size. However, grafting allows control of neither the concentration of organic groups nor of their distribution, which depends on the number of the surface silanol groups, the diffusion of reagents through the pores' channels, and steric factors. More recently, an alternative approach in one step, overcoming the main restrictions of the postsynthesis method, has been developed for the preparation of periodic hybrid materials with functionalized internal surface. It consists of the cohydrolysis and polycondensation of tetraethyl orthosilicate (TEOS) and an organotrialkoxysilane $RSi(OR')_3$ in the presence of a structure-directing agent. Mann et al, followed by some others, were the first to describe the preparation of ordered mesoporous hybrid materials by the direct synthesis method using hexadecyltrimethylammonium bromide (CTAB) under basic conditions.[12−16] This method requires that the organic

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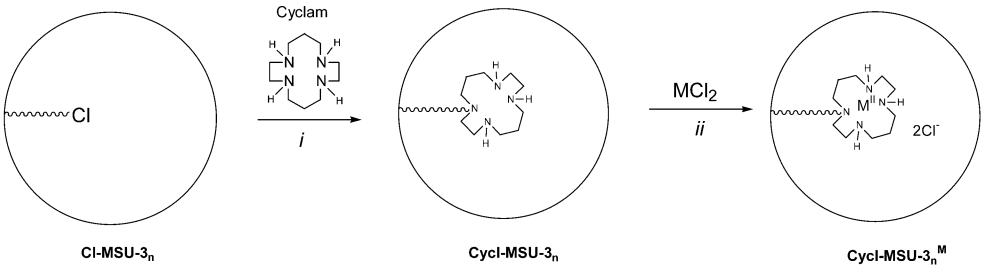
Scheme 1. Substitution of Chloro Groups in Cl−MSU-3_n by Cyclam (*i*) and Complexation of Transition Metal Ions (*ii*)



groups support basic conditions during the synthesis and acidic conditions when the surfactant is removed, which is incompatible with some organic groups. The direct synthetic approach in the presence of cationic surfactant has also been investigated under acidic conditions. In this case, weak interactions exist between the surfactant and the silicate framework, which allows removing of the surfactant by a simple solvent extraction using pure ethanol.[17]

Several groups explored the nonionic assembly route. Macquarrie prepared organically modified mesoporous materials by using primary alkylamine as structure-directing agent.[18−21] This route was extensively studied and used by other groups.[22−26] Likewise, Richer and Mercier have described the direct synthesis of functional mesoporous silica by using alkylpoly(ethylene oxide)s as structure-directing agents.[27,28] In both cases, the neutral S°I° assembly pathway results mostly in worm-like mesostructured materials with possibility of high functional group loadings. Furthermore, it is important to stress that the use of a self-assembly strategy without strong electrostatic interactions allows the complete removal of the surfactant by nondestructive solvent extraction.

Finally, the triblock copolymer $EO_{20}PO_{70}EO_{20}$ P123 [poly(ethyleneoxide)-poly(propyleneoxide)-poly(ethyleneoxide)] was proved to be very convenient under acidic conditions for the preparation of functionalized silica with hexagonal mesoscopic order.[29−31] The resulting materials have large uniform pore sizes, high surface areas, and high thermal and hydrothermal stabilities.

In this paper, we explore the chemistry permitting introduction of strongly chelated transition metal ions inside the channel pores of mesoporous hybrid materials by using the direct synthetic approach in the presence of nonionic surfactant. Indeed, the access to materials incorporating transition metal ions is of great interest as they can be a route to materials with interesting properties such as magnetism, conductivity, optic, catalytic, or gas sorption properties. For that purpose, we chose to incorporate cyclam moieties within the channel pores of mesoporous silica, the 1,4,8,11-tetraazacyclotetradecane, which is called “cyclam.” Cyclam is known for its remarkable binding ability toward transition metal ions such as copper(II), cobalt(II), nickel(II), etc.[32,33]

To select the best materials for the anchorage of chelating units in the channel pores, we first studied the preparation of mesoporous silica containing chloropropyl groups by the direct synthetic approach and using three families of nonionic surfactants (*n*-hexadecylamine, tergitol 15-S-12, and the triblock copolymer P123). The substitution of chloro groups by cyclam within these different materials, as well as the mode of anchorage of cyclam moieties, was investigated. We show that it is possible to anchor almost quantitatively cyclam moieties within the materials prepared in the presence of the triblock copolymer P123 without modification of the mesostructure (Scheme 1). The binding ability of cyclam units was tested with $CuCl_2$ and $CoCl_2$. It was found to be maintained within the materials. All the cyclam moieties located within the pores’ channels of these materials are accessible, leading to materials incorporating strongly chelated transition metal ions.

Experimental Section

All reactions were carried out under argon by using a vacuum line. Solvents were dried and distilled just before use. *n*-Hexadecylamine ($C_{16}H_{33}NH_2$), tergitol 15-S-12 ($C_{15}H_{33}EO_{12}$), triblock copolymer ($EO_{20}PO_{70}EO_{20}$ with PEO = poly (ethylene oxide) and PPO = poly (propylene oxide)), Pluronic P123, 3-chloropropyltrimethoxysilane, and tetraethyl orthosilicate (TEOS) were purchased from Aldrich and used as supplied. $CuCl_2$ and $CoCl_2$ were purchased from Acros and dried before use. 1,4,8,11-Tetraazacyclotetradecane (cyclam) was obtained from LIMSAG (UMR 5633, Université de Bourgogne, 6, Boulevard Gabriel, 21100 Dijon, France). The CP MAS ^{29}Si solid-state NMR spectra were recorded on a Bruker FTAM 300 and a CP MAS ^{13}C solid-state NMR spectra, in the latter case by using the TOSS technique. In both cases, the repetition time was 5 and 10 s with contact times of 5 and 2 ms. Chemical

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shifts (δ, ppm) were referenced to $\mathrm{Me_4Si}$. Specific surface areas were determined by the Brunauer−Emmett−Teller (BET) method on a Micromeritics ASAP 2010 analyzer, and the average pore diameters were calculated by the BJH method. Elemental analyses were carried out by the Service Central de Micro-Analyze du CNRS (Vernaison, France).

Preparation of Materials. The materials containing chloropropyl groups were prepared using the so-called direct method, i.e., co-condensation of the primary building blocks (3-chloropropyltrimethoxysilane and TEOS) in the presence of the appropriate surfactant.

Preparation of Cl−HMS$_9$. A solution of *n*-hexadecylamine (3.25 g, 13.45 mmol) in water (23 mL) and ethanol (28 mL) was added to a mixture of 3-chloropropyltrimethoxysilane (0.90 g, 4.48 mmol) and tetraethyl orthosilicate (8.40 g, 40.32 mmol). The resulting mixture was then heated at 35 °C. There wasrapid formation of a white precipitate. The suspension was kept at 35 °C for 2 d. The white precipitate was recovered by filtration and washed 3× with ethanol. The surfactant was removed by Soxhlet extraction over ethanol for 1 d. After drying at 120 °C overnight under vacuum, 3.0 g (100%) of **Cl−HMS$_9$** was obtained as a white powder. $S_{\mathrm{BET}} = 940\ \mathrm{m^2\ g^{-1}}$.^{13}C NMR (d, 75 MHz, CP-MAS): 9.2 ($C\mathrm{H_2Si}$), 16.7 ($C\mathrm{H_3CH_2OSi}$), 26.3 ($C\mathrm{H_2CH_2Si}$), 47.2 ($\mathrm{Cl}C\mathrm{H_2}$), 58.3 ($\mathrm{CH_3}C\mathrm{H_2OSi}$). ^{29}Si NMR (d, 60 MHz, CP-MAS): −65.8 ($\mathrm{T^3}$), −101.0 ($\mathrm{Q^3}$), −110 ($\mathrm{Q^4}$). IR ($\mathrm{cm^{-1}}$, KBr): 3450 (n H-bonded Si−OH), 2981−2910 (n $\mathrm{C_{sp3}}$−H), 1636 ($\mathrm{H_2O}$ bonded), 1150−1000 (n Si−O−Si).

Preparation of Cl−MSU-1$_9$. A 230-mL portion of aqueous solution (0.027 M) of tergitol 15-S-12 ($\mathrm{C_{15}H_{33}EO_{12}}$) was added to a mixture of tetraethyl orthosilicate (9.4 g, 45.34 mmol) and 3-chloropropyltrimethoxysilane (1.00 g, 5.04 mmol). The pH of the mixture was adjusted at 3 by addition of a concentrated chlorohydric acid solution (1.3 mL). A transparent solution was obtained after 5 min stirring and kept for 3 h at room temperature. The reaction mixture was then heated at 35 °C. A catalytic amount of NaF (84.6 mg, 2.02 mmol) was immediately added at 35 °C to induce the polycondensation.[34] A white precipitate appeared within a few minutes and the suspension was further stirred at 35 °C for 2 d. The white precipitate was recovered by filtration and washed with ethanol. The surfactant was removed by Soxhlet extraction over ethanol for 1 d. After drying at 120 °C overnight under vacuum, 3.2 g (95%) of **Cl−MSU-1$_9$** was obtained as a white powder. $S_{\mathrm{BET}} = 1360\ \mathrm{m^2\ g^{-1}}$. ^{13}C NMR (d, 75 MHz, CP-MAS): 9.3 ($C\mathrm{H_2Si}$), 16.1 ($C\mathrm{H_3CH_2OSi}$), 26.2 ($C\mathrm{H_2CH_2Si}$), 46.4 ($\mathrm{Cl}C\mathrm{H_2}$), 59.8 ($\mathrm{CH_3}C\mathrm{H_2OSi}$). ^{29}Si NMR (d, 60 MHz, CP-MAS): −66.0 ($\mathrm{T^3}$), −101.0 ($\mathrm{Q^3}$), −109.8 ($\mathrm{Q^4}$). IR ($\mathrm{cm^{-1}}$, KBr): 3450 (n H-bonded Si−OH), 2981−2909 (n $\mathrm{C_{sp3}}$−H), 1636 ($\mathrm{H_2O}$ bonded), 1200−1000 (n Si−O−Si).

It is worth noting that the same procedure (pH = 3, addition of NaF), but without formation of microemulsion, at $T = 35$ °C led to a material with a wormhole framework but with a notably lower surface area (730 $\mathrm{m^2\ g^{-1}}$), whereas at $T = 55$ °C an amorphous material was obtained.

Preparation of Cl−MSU-3$_n$ (*n* = 9, 15, and 30). The materials **Cl−MSU-3$_n$** (*n* = 9, 15, and 30) were prepared according to the same procedure. The preparation of **Cl−MSU-3$_9$** is given as an example.

The triblock copolymer ($\mathrm{EO_{20}PO_{70}EO_{20}}$) Pluronic P123 (4.0 g) was dissolved in 160 mL of an aqueous solution of HCl (pH 1.5). The resulting clear solution was then added to a mixture of 3-chloropropyltrimethoxysilane (0.84 g, 4.49 mmol) and tetraethyl orthosilicate (8.41 g, 40.41 mmol). The mixture was vigorously stirred for 3 h at room temperature until a transparent solution appeared. The solution was transferred to a hot oil bath at 60 °C, and NaF (76.0 mg, 1.80 mmol) was then immediately added to induce the polycondensation. A white precipitate appeared within a few minutes, and the resulting suspension was further stirred for 2 d at 60 °C.

It is worth noting that the experimental conditions to obtain ordered mesoporous **Cl−MSU-3$_n$** are of importance. Indeed, the preparation of materials in the presence of P123 at pH = 1.5 but without formation of microemulsion and without addition of NaF gave rise to mesoporous, amorphous materials. The same procedure but with formation of microemulsion led to a microporous, amorphous material. Finally, if the polycondensation and aging are accomplished at room temperature after addition of NaF at the microemulsion, the material is mesoporous with a narrow pore size distribution but amorphous. Thus, it is necessary to form a microemulsion, to heat it at 60 °C after addition of NaF, and to achieve the condensation and aging at this same temperature to get the ordered mesoporous materials **Cl−MSU-3$_n$**.

The resulting white powder was filtered off, and the surfactant was selectively removed by Soxhlet extraction over ethanol for 24 h. After drying at 120 °C overnight under vacuum, 2.89 g (94%) of **Cl−MSU-3$_9$** was obtained as white powder. $S_{\mathrm{BET}} = 1160\ \mathrm{m^2{\cdot}g^{-1}}$. ^{13}C NMR (d, 75 MHz, CP-MAS): 9.3 ($C\mathrm{H_2Si}$), 16.1 ($C\mathrm{H_3CH_2OSi}$), 26.4 ($C\mathrm{H_2CH_2Si}$), 46.0 ($\mathrm{Cl}C\mathrm{H_2}$), 59.8 ($\mathrm{CH_3}C\mathrm{H_2OSi}$). ^{29}Si NMR (d, 60 MHz, CP-MAS): −66.7 ($\mathrm{T^3}$), −92.0 ($\mathrm{Q^2}$), −101.4 ($\mathrm{Q^3}$), −109.4 ($\mathrm{Q^4}$). IR ($\mathrm{cm^{-1}}$, KBr): 3450 (n H-bonded Si−OH), 2981−2909 (n $\mathrm{C_{sp3}}$−H), 1636 ($\mathrm{H_2O}$ bonded), 1200−1000 (n Si−O−Si).

Cl−MSU-3$_{15}$. 2.97 g (98%) of **Cl−MSU-3$_{15}$** was obtained as a white powder. $S_{\mathrm{BET}} = 1000\ \mathrm{m^2{\cdot}g^{-1}}$. ^{13}C NMR (d, 75 MHz, CP-MAS): 9.1 ($C\mathrm{H_2Si}$), 15.9 ($C\mathrm{H_3CH_2OSi}$), 26.2 ($C\mathrm{H_2CH_2Si}$), 45.5 ($\mathrm{Cl}C\mathrm{H_2}$), 59.7 ($\mathrm{CH_3}C\mathrm{H_2OSi}$). ^{29}Si NMR (d, 60 MHz, CP-MAS): −64.5 ($\mathrm{T^3}$), −92.0 ($\mathrm{Q^2}$), −101.4 ($\mathrm{Q^3}$), −109.6 ($\mathrm{Q^4}$). IR ($\mathrm{cm^{-1}}$, KBr): 3426 (n H-bonded Si−OH), 2981−2909 (n $\mathrm{C_{sp3}}$−H), 1630 ($\mathrm{H_2O}$ bonded), 1200−1000 (n Si−O−Si).

Cl−MSU-3$_{30}$. 2.94 g (96%) of **Cl−MSU-3$_{30}$** was obtained as a white powder. $S_{\mathrm{BET}} = 810\ \mathrm{m^2\ g^{-1}}$. ^{29}Si NMR (d, 60 MHz, CP-MAS): −64.3 ($\mathrm{T^3}$), −91.7 ($\mathrm{Q^2}$), −101.2 ($\mathrm{Q^3}$), −109.0 ($\mathrm{Q^4}$). IR ($\mathrm{cm^{-1}}$, KBr): 3450 (n H-bonded Si−OH), 1630 ($\mathrm{H_2O}$ bonded), 1200−1000 (n Si−O−Si).

Reactivity of Chloropropyl Groups toward Cyclam. The substitution reactions within the different solids have been carried out according to the same procedure. The preparation of **cycl−MSU-3$_9$** is given as an example. For the other solids, only physical data are given below.

Preparation of Cycl−MSU-3$_9$. A mixture of cyclam (0.42 g, 2.09 mmol), **Cl−MSU-3$_9$** (1.00 g, 1.49 mmol) in 90 mL of acetonitrile, and triethylamine (1.1 g, 10.9 mmol) was heated under reflux and stirred for 2 d. The white solid was quantatitatively recovered by filtration and washed 5× with hot chloroform and 3× with hot ethanol to remove the excess of cyclam. After drying at 120 °C overnight under vacuum, 1.10 g (95%) of **cycl−MSU-3$_9$** was obtained as a white powder. The excess of cyclam contained in the reaction filtrate was titrated by conductimetry. $S_{\mathrm{BET}} = 627\ \mathrm{m^2\ g^{-1}}$. ^{13}C NMR (d, 75 MHz, CP-MAS): 9.8 ($C\mathrm{H_2Si}$), 26.2 ($C\mathrm{H_2CH_2N}$), 40.0 to 60.0 ($\mathrm{N}C\mathrm{H_2}$). ^{29}Si NMR (d, 60 MHz, CP-MAS): −61.9 ($\mathrm{T^2}$), −66.0 ($\mathrm{T^3}$), −101.6 ($\mathrm{Q^3}$), −110.0 ($\mathrm{Q^4}$). IR ($\mathrm{cm^{-1}}$, KBr): 3420 (n H-bonded Si−OH), 2953−2859 (n $\mathrm{C_{sp3}}$−H), 1634 ($\mathrm{H_2O}$ bonded), 1200−1000 (n Si−O−Si).

Cycl−MSU-3$_{15}$. 95% yield obtained as a white powder. $S_{\mathrm{BET}} = 688\ \mathrm{m^2\ g^{-1}}$. ^{13}C NMR (d, 75 MHz, CP-MAS): 9.7 ($C\mathrm{H_2Si}$), 26.2 ($C\mathrm{H_2CH_2N}$), 40.0 to 60.0 ($\mathrm{N}C\mathrm{H_2}$). ^{29}Si NMR (d, 60 MHz, CP-MAS): −61.9 ($\mathrm{T^2}$), −66.0 ($\mathrm{T^3}$), −99.7 ($\mathrm{Q^3}$), −108.0 ($\mathrm{Q^4}$). IR ($\mathrm{cm^{-1}}$, KBr): 3421 (n H-bonded Si−OH), 2941−2842 (n $\mathrm{C_{sp3}}$−H), 1640 ($\mathrm{H_2O}$ bonded), 1200−1000 (n Si−O−Si).

Cycl−MSU-3$_{30}$. 94% yield obtained as a white powder. $S_{\mathrm{BET}} = 464\ \mathrm{m^2\ g^{-1}}$. ^{29}Si NMR (d, 60 MHz, CP-MAS): −66.0 ($\mathrm{T^3}$), −99.8 ($\mathrm{Q^3}$), −108.1 ($\mathrm{Q^4}$).

Complexation of Copper and Cobalt Salts by Cyclam Moieties Within the Cycl−MSU-3$_n$ Materials. All the complexation reactions with **cycl−MSU-3$_n$** were carried out according to the same procedure with standard high-vacuum and dry-argon techniques. The preparation of **cycl−MSU-3$_9^{\mathrm{Cu}}$** is given as an example.

Preparation of Cycl−MSU-3$_9^{\mathrm{Cu}}$. A total of 1.00 g (1.49 mmol) of **cycl−MSU-3$_9$** was added to an ethanolic solution of $\mathrm{CuCl_2}$ (0.017 M, 123 mL). The resulting suspension was heated overnight under reflux with stirring. The solid was quantita-

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Table 1. Physicochemical Characteristics of Chloropropyl-Functionalized Mesoporous Silica

material	S_{BET} (m^2 g^{-1})	V_p (cm^3 g^{-1})	D_p[a] (Å)	d_{100} (Å)	wall thickness[b] (Å)	Si/Cl[c]	[Cl group content][c] (mmol g^{-1})
Cl−HMS$_9$	940	1.00	20	37.1	22.6	8.4 (10)	1.50
Cl−MSU-1$_9$	1360	0.90	32	43.0	17.4	10.3 (10)	1.21
Cl−MSU-3$_9$	1160	1.13	47	91.9	59.1	9.7 (10)	1.24
Cl−MSU-3$_{15}$	1000	1.05	54	96.6	57.5	17 (16)	0.87
Cl−MSU-3$_{30}$	810	1.11	61	106.5	62.0	27 (31)	0.51

[a] Calculated from the desorption branch by using the Horvath−Kawazoe model for materials **Cl−HMS$_9$** and **Cl−MSU-1$_9$**, and the BJH method for **Cl−MSU-3$_n$**. [b] Calculated by a_0 − pore size ($a_0 = \sqrt{2}d_{100}/3\wedge 1/2$). [c] Calculated from elemental analyses. In parentheses, theoretical values.

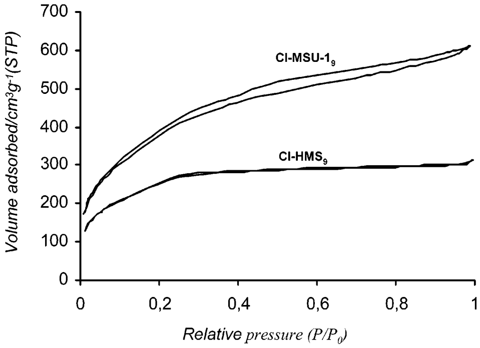

Figure 1. Nitrogen adsorption/desorption isotherms of **Cl−HMS$_9$** and **Cl−MSU-1$_9$**.

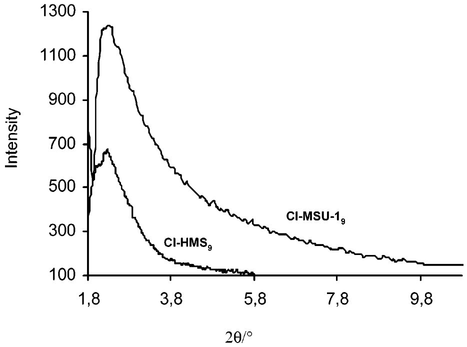

Figure 2. XRD patterns **Cl−HMS$_9$** and **Cl−MSU-1$_9$**.

tively recovered by filtration and washed with dry ethanol several times to remove the excess of copper salt. After drying at 120 °C overnight under vacuum, 1.08 g (97%) of **cycl−MSU-3$_9^{Cu}$** was obtained as a violaceous powder. The excess copper salt contained in the reaction filtrate was titrated by conductimetry. $S_{BET} = 338$ m^2 g^{-1}.

Conductometric Titration. *Titration of Cyclam.* The filtrate (obtained during the preparation of **cycl−MSU-3$_n$**) was evaporated, and the white residue was dissolved in deionized water (100 mL). A known volume of this solution (20 mL) was then titrated with an aqueous solution of copper bromide (0.012 M). The conductance value was followed after each addition of copper ion. The inflection point of the titration curve was used to determine the exact amount of cyclam contained in the starting solution.

Titration of Copper Salt. The filtrate (obtained during the preparation of **cycl−MSU-3$_n^{Cu}$**) was evaporated, and the residue was dissolved in deionized water (100 mL). A known volume of this solution (20 mL) was then titrated by an aqueous solution of cyclam (0.012 M). The conductance value was followed after each addition of cyclam. The inflection point of the titration curve was used to determine the exact amount of copper salt contained in the starting solution.

Results and Discussion

Characterization of Chloropropyl-Functionalized Mesoporous Silica by Nonionic Assembly Routes. *Chloropropyl-Functionalized Mesoporous Silica Prepared using n-Hexadecylamine ($C_{16}H_{33}NH_2$).* The cohydrolysis and polycondensation of the mixture of 3-chloropropyltrimethoxysilane with 9 equiv of TEOS in the presence of *n*-hexadecylamine as the surfactant was carried out under the experimental conditions that we have previously described.[23] The solids will be denoted **Cl−HMS$_9$** (**Cl** for the functional group, **HMS**[3,4] to recall the primary alkylamine surfactant used, and the number **9** in index to indicate the number of TEOS equiv).

The N_2 adsorption−desorption isotherm is shown in Figure 1. It is representative of a material containing micropores and small mesopores as expected.[22,23,25] The textural data are given in Table 1. It is worth noting that the surface area (940 m^2g^{-1}) and the pore volume (1 cm^3g^{-1}) of the material are large. The XRD pattern of **Cl−HMS$_9$** was characteristic (Figure 2) of wormhole motif mesostructured HMS phases as were all the materials prepared in the presence of primary alkylamine as structure-directing agent.[18−28]

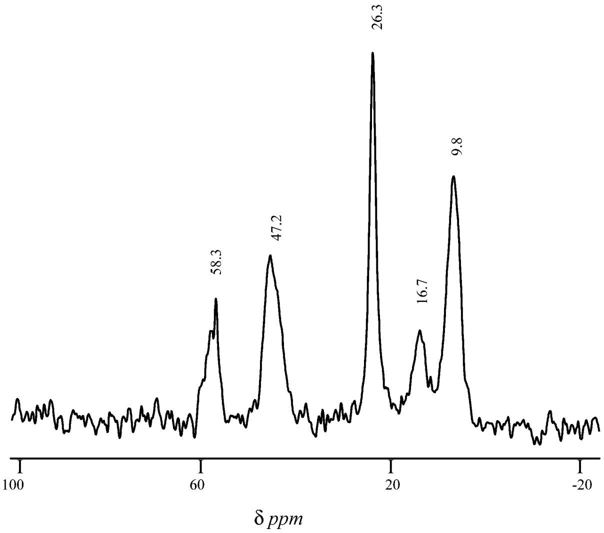

Figure 3. ^{13}C CP MAS NMR (solid state) spectrum of **Cl−HMS$_9$**.

Solid-state ^{13}C MAS NMR spectrum (Figure 3) of the extracted material confirmed that the organic group is undamaged, and confirms complete removal of the surfactant (see Experimental Section). It exhibits also some signals indicating the presence of remaining ethoxy groups. Solid-state ^{29}Si MAS NMR spectrum of **Cl−HMS$_9$** displayed signals at − 100.5 ppm and − 109.9 ppm attributed at the substructures Q^3 and Q^4, respectively, denoting high cross-linking of the siloxane species. An additional signal at − 65.9 ppm assigned at the substructure T^3 showed the fully cross-linked organosilsesquioxane species.

The extent of the organic moieties incorporation into **Cl−HMS$_9$** was inferred from the results of the elemental analyses of Si and Cl. As indicated in Table 1, the ratio Si/Cl was found to be 8.4, whereas the value based on components concentrations used initially in the synthesis was 10, which shows a rather good incorporation of the organic group giving rise to a large content of organic group (1.50 mmol g^{-1}).

Chloropropyl-Functionalized Mesoporous Silica Prepared Using Tergitol 15-S-12 ($C_{15}H_{31}(OCH_2-CH_2)_{12}-OH$). The cohydrolysis and polycondensation of the mixture of 3-chloropropyltrimethoxysilane with 9 equiv of TEOS using nonionic alkylpoly(ethylene oxide) surfactant as structure-directing agent, namely Tergitol 15-S-12, was achieved according to a procedure that was inspired by that described by Prouzet et al. giving rise to **MSU-1** silica.[34] This procedure involved two steps: the first step consisted of mixing the nonionic surfactant and TEOS under acidic conditions to obtain a microemulsion. The second step was the addition of a catalytic amount of fluoride ion to induce the polycondensation. The main feature of this approach comes from the formation of a microemulsion at pH 3, which is a stable solution containing monodisperse globules. Furthermore, separation of the assembly step from the polycondensation increases the interaction between the silica source and the surfactant, which is favorable to a better structuration. We have adapted this procedure to the preparation of the hybrid material, the microemulsion containing both the organosilane and TEOS. The importance of the procedure is given in the Experimental Section. The resulting material was named **Cl−MSU-1$_9$** for reasons similar to those explained for **Cl−HMS$_9$**: **Cl** for 3-chloropropyltrimethoxysilane, **MSU-1**[5,34] recalling the name of the silica prepared in the presence of tergitol 15-S-12, and **9** in index to specify the ratio of organosilane/TEOS, which was 1:9.

The N_2 adsorption−desorption isotherm for **Cl−MSU-1$_9$** (Figure 1) was characteristic of a mesoporous solid with a rather broad pore size distribution. The surface area was found to be very large (1360 m^2 g^{-1}) as was the pore volume (0.90 cm^3 g^{-1}). The mean pore diameter was found to be larger than that of **Cl−HMS$_9$** (Table 1).

The powder X-ray pattern for **Cl−MSU-1$_9$** exhibits a single low-angle peak (Figure 2) characteristic of a wormhole framework with a d spacing of 43.0 Å, whereas for **Cl−HMS$_9$** it was 37.1 Å.

The solid-state ^{13}C MAS NMR spectrum of **Cl−MSU-1$_9$** is similar to that of **Cl−HMS$_9$.** It exhibits distinctly the three signals assigned to the propyl group as well as those of some remaining ethoxy groups.

The solid-state ^{29}Si MAS NMR spectrum of **Cl−MSU-1$_9$** is also very similar to that of **Cl−HMS$_9$** (signals at −101.0 ppm and −109.8 ppm attributed at the substructures Q^3 and Q^4, respectively, and an additional signal at −66.0 ppm assigned at the substructure T^3).

The ratio Si/Cl resulting from the elemental analyses of Si and Cl was found to be 10.3, which is very close to the theoretical ratio (10). That corresponds to content in organic group of 1.21 mmol g^{-1}.

Chloropropyl-Functionalized Mesoporous Silica Prepared Using Pluronic 123 ($EO_{20}PO_{70}EO_{20}$). The cohydrolysis and polycondensation of 3-chloropropyltrimethoxysilane with n equiv of TEOS (n = 9, 15, 30) using nonionic Pluronic 123 as structure-directing agent was achieved according to a two-step procedure as for **Cl−MSU-1$_9$**: formation of a microemulsion at pH = 1.5 at room temperature, then addition of NaF to the mixture, which was heated at 60 °C. After aging at 60 °C for 2 days and removal of the P123 (see experimental), the solids **Cl−MSU-3$_n$** were obtained (**MSU-3** to recall the first preparation of silica in the presence of bloc-copolymer).[5]

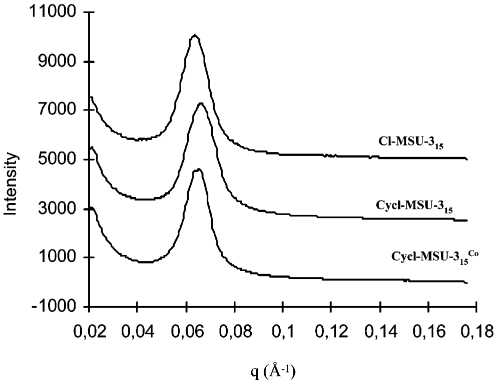

Figure 4. Small-angle X-ray scattering patterns of **Cl−MSU-3$_{15}$**, **Cycl−MSU-3$_{15}$**, and **Cycl−MSU-3$_{15}^{Co}$**. To allow a better comparison, the data for **Cycl−MSU-3$_{15}$** and **Cl−MSU-3$_{15}$** were shifted by 2500 and 5000 units, respectively.

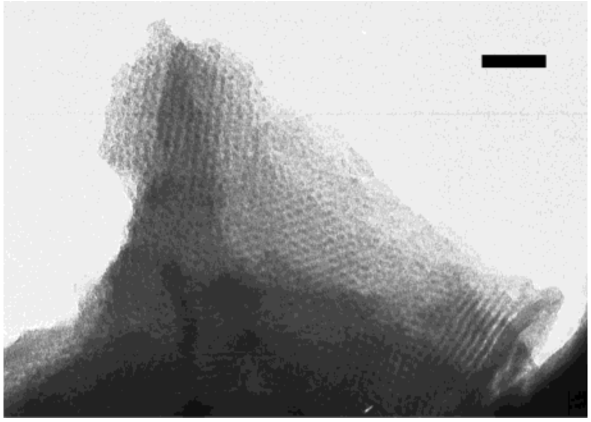

Figure 5. TEM image of **Cl−MSU-3$_9$** after surfactant extraction. Scale bar = 50 nm.

The composition of the final materials was inferred from the results of elemental analyses of Si and Cl. They were found to be close to those for the original mixtures as indicated in Table 1.

Small-angle X-ray scattering patterns of different samples exhibit single d_{100} reflections (Figure 4). Higher-order Bragg reflections were not resolved. Values of the structural parameters d_{100} are listed in Table 1. It is worth noting that the intensity of the peak is lower for the material containing the highest concentration of organic group. That is probably due to a higher contrast matching effect arising from the material with the most organic group. A TEM image of the material **Cl−MSU-3$_9$** is shown in Figure 5 providing evidence for a 2D hexagonal structure. The importance of the order of introduction of the reagents to obtain ordered materials is given in the Experimental Section.

The N_2 adsorption−desorption isotherms of materials **Cl−MSU-3$_n$** are very similar. They are type IV isotherms, characteristic of mesoporous materials with a

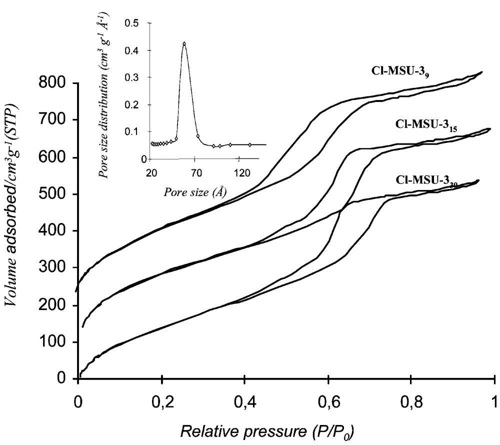

Figure 6. Nitrogen adsorption/desorption isotherms of **Cl−MSU-3$_9$**, **Cl−MSU-3$_{15}$**, and **Cl−MSU-3$_{30}$**, and BJH pore size distribution plot (inset) of **Cl−MSU-3$_{30}$**. To allow a better comparison, the data for **Cl−MSU-3$_9$** and **Cl−MSU-3$_{30}$** were shifted by +100 and −100 cm^{3}g^{-1}, respectively.

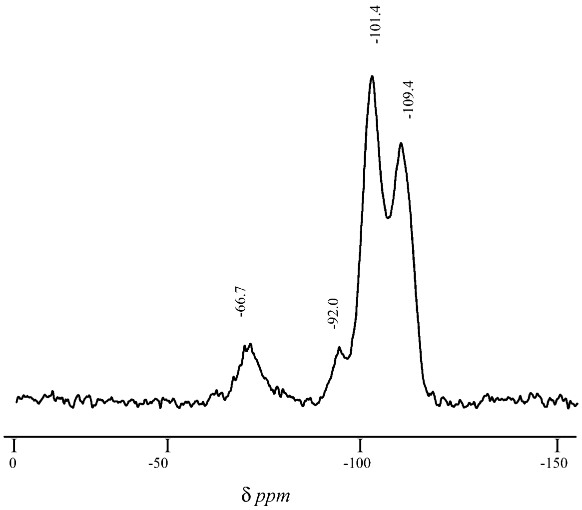

Figure 7. ^{29}Si CP MAS NMR (solid state) spectrum of **Cl−MSU-3$_9$**.

narrow pore size distribution (Figure 6). The textural data of materials are given in Table 1. The S_{BET}, pore volumes, and mean pore diameters of these materials are very large, with the mean pore diameters increasing as the loading in organic groups was decreasing. The mean thickness of the pore walls estimated from the d_{100} spacing and the mean pore size is large as observed for organic-functionalized SBA-15 silica.[29,30]

Solid-state ^{13}C MAS NMR spectra of materials **Cl−MSU-3$_n$** are similar to those of **Cl−HMS$_9$** and **Cl−MSU-1$_9$**. They display distinctly the three signals assigned to the propyl group (9.1, 26.2, and 45.5 ppm) as well as those of some remaining ethoxy groups (15.9 and 59.7 ppm).

The solid-state ^{29}Si MAS NMR spectra of materials **Cl−MSU-3$_n$** exhibit a signal at − 66.7 ppm, assigned to the substructure T^3, as well as signals of siloxanes (at −92.0, −101.4, and −109.6 ppm attributed, respectively, to the substructures Q^2, Q^3, and Q^4) (Figure 7).

Study of the Accessibility and Reactivity of Chloropropyl Groups Within Materials Cl−HMS$_9$, Cl−MSU-1$_9$, and Cl−MSU-3$_9$. We studied the accessibility and the reactivity of chloropropyl groups located within the channel pores of materials **Cl−HMS$_9$**, **Cl−MSU-1$_9$**, and **Cl−MSU-3$_9$**.

Table 2. Experimental Conditions for the Nucleophilic Substitution of the Chloro Group by the Cyclam Moiety

starting sample	D_p[a] (Å)	solvent[b]	time (h)	equiv of cyclam	% of Cl substituted[c]
Cl−MSU-1$_9$	32	toluene	48	10	59
Cl−MSU-1$_9$	32	CH_3CN	12	1	51
Cl−MSU-1$_9$	32	CH_3CN	48	1	100
Cl−MSU-3$_9$	47	CH_3CN	12	1	69
Cl−MSU-3$_9$	47	CH_3CN	24	1	69
Cl−MSU-3$_9$	47	CH_3CN	48	5	100
Cl−MSU-3$_9$	47	CH_3CN	48	1	96

[a] Calculated from the desorption branch by using the Horvath−Kawazoe model for materials **Cl−MSU-1$_9$** and the BJH method for **Cl−MSU-3$_n$**. [b] Solvent heated under reflux. [c] Calculated from elemental analyses.

Table 3. Study of the Substitution Mode of Cyclam Moieties as a Function of Pore Diameters

starting sample	D_p (Å)	% of Cl substituted[a]	% of mono substitution[a]	% of di substitution[a]
Cl−HMS$_9$	20	50	100	0
Cl−MSU-1$_9$	32	100	50	50
Cl−MSU-3$_9$	47	80	100	0

[a] Calculated from elemental analyses.

First, the substitution reaction of chloro groups by cyclam moieties (Scheme 1) within the materials **Cl−MSU-1$_9$** and **Cl−MSU-3$_9$** was investigated under different experimental conditions (solvent, temperature, reaction time, equivalents of cyclam) (Table 2). The excess of cyclam remaining in solution was determined by conductometric measurement, which allowed inferring the percentage of chloro groups substituted. This percentage was also deduced from the results of elemental analyses of N and Cl of materials after reaction. These data allowed finding that the percentage of substitution of chloro groups by cyclam moieties was quantitative in acetonitrile heated under reflux for 48 h in the presence of at least 1 equiv of cyclam.

Following this result, we have investigated the degree of substitution of cyclam as a function of the mean pore size of materials **Cl−HMS$_9$**, **Cl−MSU-1$_9$**, and **Cl−MSU-3$_9$**. For that purpose, 1.4 equiv of cyclam was mixed with the material in acetonitrile heated under reflux for 48 h. The excess of cyclam remaining in the filtrate was titrated by conductimetry as previously described. The results of elemental analyses of N and Cl of materials after reaction were compared with those of the elemental analyses of the same elements before reaction. The whole data led to the following results (Table 3): under exactly the same experimental conditions, only 50% of chloropropyl groups were substituted from the material **Cl−HMS$_9$** (D_p= 20 Å), whereas 100% of chloro groups were substituted within materials **Cl−MSU-1$_9$** and 80% from **Cl−MSU-3$_9$**. Furthermore, it was found that the anchoring of cyclam occurs only by monosubstitution within the materials **Cl−HMS$_9$** and **Cl−MSU-3$_9$,** while it occurs by both monosubstitution and disubstitution in almost equal ratio within **Cl−MSU-1$_9$** (Scheme 2).

These results show the importance of the pore size to achieve a chemical transformation on a functional group located within the channel pores. In the material **Cl−HMS$_9$** only 50% of Cl groups are substituted because

Scheme 2. Anchoring Mode of Cyclam Within Cycl−HMS, Cycl−MSU-1, and Cycl−MSU-3

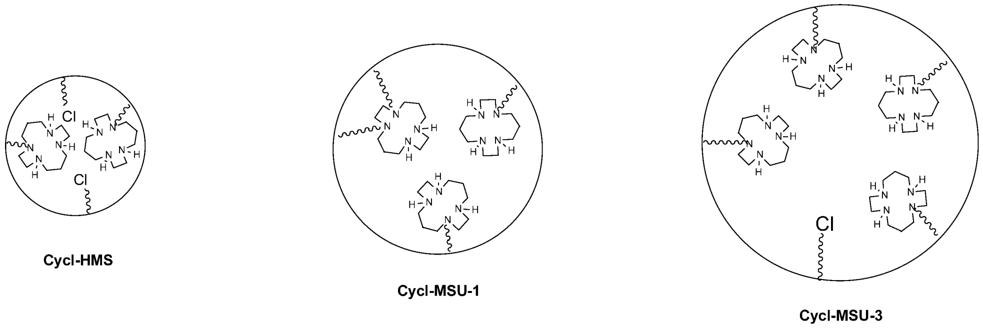

Table 4. Physicochemical Characteristics of Cyclam-Functionalized Mesoporous Silica

sample	S_{BET} ($m^2\ g^{-1}$)	V_p ($cm^3\ g^{-1}$)	D_p[a] (Å)	d_{100} (Å)	a_o (Å)	wall thickness (Å)	[cyclam][b] mmol g^{-1}	% of substitution	
								μ.anal. [c]	titration
cycl−MSU-3$_{9}$	627	0.52	36	92	106	70	0.93	80	80
cycl−MSU-3$_{15}$	688	0.76	47	100	115	68	0.70	92	92
cycl−MSU-3$_{30}$	464	0.82	61	106	122	61	0.48	98	95

[a] Calculated from the desorption branch by using the BJH method. [b] Calculated from the elemental analyses. [c] Calculated from conductimetry measurements.

of the very small mean pore size ($D_p = 20$ Å). However, this low ratio of substitution allows the anchorage of the cyclam by monosubstitution exclusively. 100% of Cl groups are substituted within the material **Cl−MSU-1$_{9}$** in which the mean pore diameter is 32 Å, but anchoring of cyclam takes place by both mono- and disubstitution, probably because of the close proximity of chloro groups inside the pores. Finally, the percentage of substitution of chloro groups is high and occurs essentially by monosubstitution inside the channel pores of **Cl−MSU-3$_{9}$** because of the large pore size. ($D_p = 47$ Å). The absence of anchoring of cyclam by disubstitution within **Cl−MSU-3$_{9}$** is a good indication of the regular distribution of organic groups within the pore channels of the material. It is worth noting that this is one of the main characteristics of the materials prepared by the direct synthetic approach.[22]

Study of the Reactivity of Chloropropyl Groups Within Materials Cl−MSU-3$_n$ (n = 9, 15, 30). Taking into account the results previously described, we have studied the substitution of chloro groups by the cyclam within the different materials **Cl−MSU-3$_{n}$** (n = 9, 15, 30), which are the more appropriate for this reaction. That was achieved by treating the solids **Cl−MSU-3$_{n}$** with an acetonitrile solution containing 1.4 equiv of cyclam heated under reflux for 48 h in the presence of a large excess of triethylamine (Scheme 1). The solids were then filtered off and copiously washed with hot methanol, acetone, and ether to afford **cycl−MSU-3$_{n}$**. Some relevant physical data of the solids are given in Table 4.

The content of cyclam moieties and the % of substitution were determined by titration of the excess of cyclam by conductimetry measurement. These results (Table 4) were confirmed by the elemental analyses of Si, Cl, and N. Thus, the substitution was almost quantitative, except for the material with the highest concentration of organic group, i.e., **Cl−MSU-3$_{9}$**, for which the % of substitution was about 80%. That is probably due to steric constraints. Thus, the chloro groups in the materials of **Cl−MSU-3$_{n}$** are mostly accessible due to the rather large mean pore size.

Solid-state ^{13}C MAS NMR spectra of materials **cycl−MSU-3$_{n}$** are similar. They display two signals at 9.8 ppm and 26.2 assigned, respectively, to carbon atoms in α from the silicon atom and in β from nitrogen atoms. They exhibit also a broad signal between 40 and 60 ppm attributed to carbon atoms in α from the nitrogen atoms.

The solid-state ^{29}Si MAS NMR spectra of materials **cycl−MSU-3$_{n}$** are very similar to those of the corresponding starting materials **Cl−MSU-3$_{n}$**.

SAXS patterns of different samples **cycl−MSU-3$_{n}$** are very similar to those of the starting materials. They exhibit the diffraction peak corresponding to the same d_{100} spacing as those of the starting materials indicating that the hexagonal structure of materials was maintained (Figure 4). The N_2 adsorption−desorption isotherms for **cycl−MSU-3$_{n}$** are of type IV, characteristic of mesoporous materials with a narrow pore size distribution. The surface area, total pore volume, and pore size decreased notably after anchoring as expected,[35] which is consistent with the presence of a significant amount of anchored species. Thus, it is possible to incorporate almost quantitatively a rather bulky group without modification of the structure and with minor modification of the texture. The sequence: direct synthesis method of ordered mesoporous hybrid materials containing Cl groups followed by the almost quantitative substitution of chloro groups by cyclam moieties led to materials containing cyclam propyl moieties regularly distributed within the channel pores. It is worth noting that it is not possible to obtain the materials **cycl−MSU-3$_{n}$** in one step by cohydrolysis and polycondensation of *N*-triethoxysilylpropylcyclam[36] and TEOS in the presence of P123. That points out the interest to achieve chemical transformation within hybrid materials without modification of the structure.

Complexation of Copper(II) and Cobalt(II) Salts by Cyclam Moieties Within Cycl−MSU-3$_{n}$. We next investigated complexation reaction of $CuCl_2$ and $CoCl_2$

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(35) Sorokin, A. B.; Tuel, A. *New J. Chem.* **1999**, *23*, 473.

(36) Mehdi, A.; Denat, F.; Barbette, F.; Guilard, R.; Lagrange, G. *World Pat.* WO 9937399, 1999.

Table 5. Physicochemical Characteristics of Metal/Cyclam-Functionalized Mesoporous Silica

sample	molar ratio[a] N/M (th.:4)	[metal] mmol g^{-1} elem. anal.	[metal] mmol g^{-1} (X-fluorescence)	[metal] mmol g^{-1} (conduct. meas.)	S_{BET} (m^2 g^{-1})	D_p (Å)	V_p (cm^3 g^{-1})
cycl−MSU-3$_{9}^{Cu}$	4.1	0.78	0.76	0.77	338	35	0.40
cycl−MSU-3$_{15}^{Cu}$	4.0	0.66	0.60	0.62	568	46	0.76
cycl−MSU-3$_{30}^{Cu}$	3.9	0.54	0.45	0.50	575	61	0.82
cycl−MSU-3$_{9}^{Co}$	3.9	0.76	-	0.80	453	35	0.72
cycl−MSU-3$_{15}^{Co}$	3.9	0.65	-	0.62	677	46	0.73
cycl−MSU-3$_{30}^{Co}$	4.0	0.33	-	0.40	463	54	0.71

[a] Calculated from the elemental analyses.

by the cyclam moieties located inside the pore channels of materials **cycl−MSU-3$_n$** (n = 9, 15, 30) (Scheme 1). The materials **cycl−MSU-3$_n$** were treated with an excess of anhydrous $CuCl_2$ or $CoCl_2$ (1.4 equiv. of Cu^{II} or Co^{II} per cyclam moieties) in ethanol heated under reflux for 24 h. The resulting solids that were named **cycl−MSU-3$_n^M$** (M = Cu or Co) were copiously washed with ethanol to eliminate the noncomplexed salt. The filtrate containing the excess of salt was titrated by conductimetry measurements (see Experimental Section). Elemental analyses of metal and nitrogen, and titrations by X-fluorescence for copper were done. It is worth noting that a good concordance of these data was obtained (Table 5). The ratio of M^{II} per cyclam moieties was inferred from these results. It was found to be close to 1/1, which shows that all the cyclam moieties are accessible for complexation.

The results of the analysis of the adsorption−desorption isotherms for the materials **cycl−MSU-3$_n^M$** (M = Cu or Co) are summarized in Table 5. In all cases, the isotherms are similar to those of starting materials, i.e., they are of type IV, characteristic of mesoporous materials with a narrow pore size distribution. Starting from a given material, the decrease in textural data (surface area, total pore volume, and pore size) is in the same range for both salts. As would be expected, it is notable in particular for the more concentrated material in cyclam moieties (**cycl−MSU-3$_9$**).

SAXS patterns of different samples after complexation are very similar to those of the starting materials (Figure 4). The diffraction peaks appear for the same diffraction angle as for the starting materials and for the same d_{100} spacing, indicating that the structure of the materials is maintained after the different chemical transformations within the materials. As it was previously observed for the starting materials, the intensity of the peak is notably lower for the materials **cycl−MSU-3$_{15}^{Co}$** and **cycl−MSU-3$_{9}^{Co}$** than for **cycl−MSU-3$_{30}^{Co}$** (Figure 8). That is probably due to a higher contrast matching effect arising from the material with the highest content in organic group.

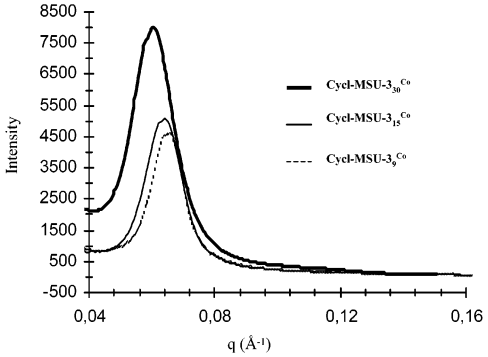

Figure 8. Small-angle X-ray scattering patterns of **Cycl−MSU-3$_{9}^{Co}$**, **Cycl−MSU-3$_{15}^{Co}$**, and **Cycl−MSU-3$_{30}^{Co}$**.

Conclusion

In this paper, we describe the chemistry permitting incorporation of strongly chelated transition metal ions inside mesoporous silica. Three families of mesoporous silica containing chloropropyl groups prepared by the direct synthetic approach using nonionic assembly routes were described. The study of the anchoring of cyclam moieties within the channel pores of these functionalized mesoporous silica showed differences in the degree of substitution of cyclam moieties according to the mean pore size of these different materials. The materials prepared by using the Pluronic P123 were found to be the most convenient to anchor cyclam moieties due to the rather large pore size. In this case, anchoring of cyclam units occurred almost quantitatively and without modification of the mesostructure. Evidence for monosubstitution of cyclam was given, which is a good indication of the regular distribution of chloropropyl groups inside the channel pores. Subsequent complexation of $CuCl_2$ and $CoCl_2$ was achieved showing that all the cyclam moieties located inside the channel pores are accessible. The method is general and can be extended to others transition metal or lanthanide ions.

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