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Cyclam complexes containing silica gels for dioxygen adsorption

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Several cyclam incorporating silica gels have been synthesised using three different methods, including a sol–gel approach. These various materials show different textures and the macrocycle contents can reach values up to 1.5 mmol g^{-1}. Cu(II) and Co(II) complexes of these modified silica gels have been studied. Finally, the efficiency of $[Co(cyclam)]^{2+}$ grafted onto silica for binding dioxygen has been determined using ESR spectroscopy and static volumetric gas uptake measurements. The most efficient material behaves as a high-performance dioxygen binding system, showing a very high affinity for dioxygen ($(P_{1/2})_1 = 1.91$ Torr) coupled with a large total volume of gas adsorbed at 1 atm (3.0 cm^3 g^{-1}).

Introduction

Saturated polyazamacrocycles have long been known to form stable complexes with various guests.[1] 1,4,8,11-Tetraazacyclotetradecane (cyclam) and its N-substituted derivatives have been particularly studied.[2] Numerous works have been devoted to the capacity of cyclam and related compounds to bind transition metal cations. In order to prepare new classes of ion exchangers for specific separations, polyazacycloalkanes have been incorporated onto both organic and inorganic polymers.[3,4] Such materials have been used in solid–liquid extractions in the field of metal recovery or waste water treatment. The main advantage of this approach is to avoid the loss of the ligand observed in liquid–liquid extraction processes. Immobilisation of metal complexes in porous materials provides favourable conditions for reversible addition of dioxygen from air, by decreasing the rate of the metal irreversible oxidation and preventing dimerisation to form a μ-peroxo complex. In order to prepare stable dioxygen binding cobalt(II) complexes, metal derivatives were immobilised on various inorganic supports. For example amine,[5] cyanide,[6,7] polypyridine,[8,9] Schiff bases,[10–13] and porphyrin[14] cobalt complexes have been incorporated in the cavities of zeolites[7,9] or mesoporous silica.[13] However, the coordination scheme of the cobalt ion is not easily controlled and the materials are usually poorly loaded. Silica immobilised cyclam cobalt complexes should be good candidates for the selective coordination of dioxygen because it is known that cobalt tetraazacycloalkane complexes have a great affinity for dioxygen in solution.[15,16] Moreover, silica gel has been used in applications ranging from heterogeneous catalysis to trace analysis[17] but little is known concerning the fixation of dioxygen on complexes grafted on silica.[13,18] The chemical modification of silica gel generally involves the reaction of silanol groups with silanizing reagents.[19] Another route for the preparation of modified silica gels results from the sol–gel condensation of organic precursors bearing hydrolysable groups such as $Si(OR)_3$.[20] Recently, we reported the synthesis of new organic–inorganic hybrid materials starting from a tetrasilylated cyclam.[21] We describe here three different preparations of cyclam containing silica gels in which the macrocycle is covalently bound to the support *via* one nitrogen atom. The first two methods involve the modification of a commercial silica gel while the latter is the cogelification of a monosilylated cyclam and tetraethoxysilane. The texture, the macrocycle content, the copper and cobalt uptake capacities of these materials are discussed. Finally the thermodynamic data relative to dioxygen binding by the silica gels containing $[Co(cyclam)]^{2+}$ have been determined from the adsorption isotherms using static volumetric gas uptake measurements. ESR spectroscopy was also used for the characterisation of the oxygenated species.

Results and discussion

Influence of the grafting method on the characteristics of the material

Cyclam content. The amount of cyclam grafted by Method 1 (Scheme 1), determined by nitrogen elemental analysis, does not exceed 0.38 mmol per gram of silica gel (Table 1, entry 2). This value is significantly lower than the chlorine content before reaction with the macrocycle (Table 1, entry 1), showing that the nucleophilic substitution reaction is not complete. Moreover, the quantity of chlorine atoms remaining in the final material does not fit the difference between the initial concentration of chlorine and the amount of grafted cyclam (Table 1, entry 2). Indeed, some cyclam moieties are certainly linked to the silica gel by more than one nitrogen atom (84% if only disubstitution occurs). Obviously, the presence of residual chlorine can be prejudicial to the use of such material for some applications. Even more important is the polysubstitution of some macrocycles because the influence of the number of substituents on the properties of the ligand is well established. These two main drawbacks led us to investigate other approaches for the synthesis of silica immobilised macrocycles.

One way to overcome the presence of unreacted chlorinated arms on the material is to introduce the linker on the macrocycle before grafting on silica gel. Method 2 is more synthetically demanding because the first step is the selective mono N-functionalisation of cyclam with iodopropyltriethoxysilane.[22] However, this step is performed in a good yield by using an excess of cyclam (5 equiv.) in order to avoid the formation of polysubstituted tetraazacycloalkanes. The monosilylated cyclam is grafted according to Method 1. The material obtained *via* Method 2 contains no chlorine atom and only monosubstituted macrocycles are linked to the solid. Nitrogen elemental analysis gives values up to 0.81 mmol g^{-1} for macrocycle content in such materials (Table 1, entry 3). It has also to be noted that the amount of grafted cyclam increases linearly with the amount of monosubstituted cyclam used for the reaction until around 0.70 mmol g^{-1} (Fig. 1). Then the

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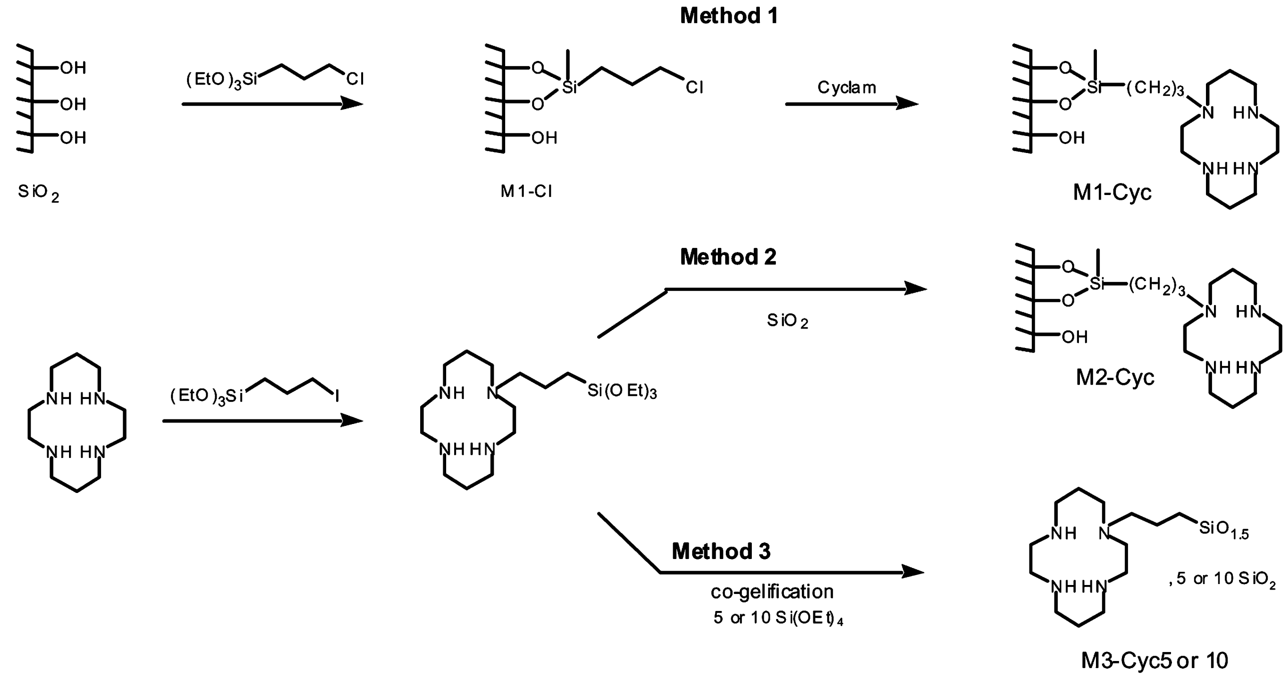

Scheme 1 Different methods of attachment.

Table 1 Cyclam and chlorine contents (mmol g^{-1}) determined by elemental analysis

Entry	Method of attachment	Material	Cyclam content/ mmol g^{-1}	Chlorine content/ mmol g^{-1}
1	1	M1-Cl	0	1.08
2	1	M1-Cyc	0.38	0.38
3	2	M2-Cyc	0.81	0
4	3	M3-Cyc5	1.54	0
5	3	M3-Cyc10	0.97	0

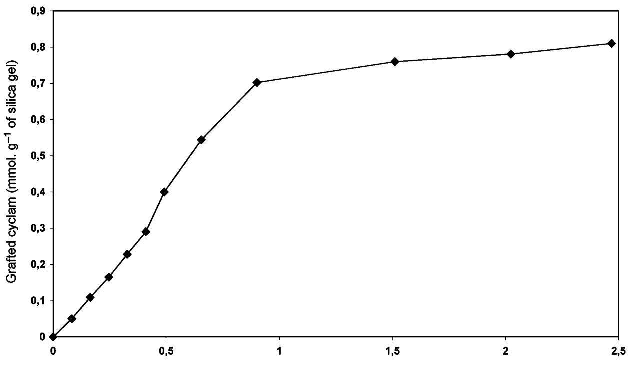

Fig. 1 Grafted cyclam as a function of the amount of cyclam used for the reaction.

curve shows a slight increase in spite of the significant addition of precursor during the grafting step. A concentration of 1 mmol of cyclam per gram of silica gel during this reaction is a compromise between a good loading of the silica gel and a reasonable ratio of grafted cyclam : cyclam used. The macrocycle content is considerably increased when compared to the material obtained *via* Method 1.

An alternative to the modification of silica gel is to incorporate the organic moiety during the silica preparation. Numerous works have been devoted to the synthesis of hybrid organic–inorganic materials using sol–gel techniques.[23] This methodology often involves the cogelification of tetraethoxysilane (TEOS) with a trialkoxysilane containing the desired organic group. The monosilylated cyclam used in Method 2 is a precursor of such materials. A mixture of the functionalised macrocycle and TEOS is hydrolysed with a stoichiometric amount of water in the presence of 1% TBAF as a catalyst. Two hybrid materials have been prepared using two different TEOS : functionalised cyclam ratios. This procedure leads to materials containing up to 1.5 mmol of cyclam per gram (Table 1, entries 4 and 5). It is noteworthy that such a material contains around 30% w/w of cyclam. The texture of the silica gel obtained by this route is not predictable but a good reproducibility in terms of porosity and specific area is attained when the experimental conditions are similar: nature of the catalyst, solvent, concentration of reagents, and external parameters such as temperature, pressure or sonication.

Textural characteristics. The specific area and the porosity of all the materials have been determined in order to study the influence of the grafting method on the texture of the solid (Table 2). The CP/MAS^{29}Si NMR characteristics of the solids are also given in Table 2. The presence of T substructures is an evidence of the grafting on silica gel. The comparison between entries 1,2,3 (Method 1) or 1,4,5 (Method 2) in Table 2 proves that the modification of the silica gel surface implies a decrease of both the surface area and the porosity. This is a general feature observed during the grafting of organic moieties onto silica gels.[17] The materials obtained by Methods 1 and 2 exhibit nitrogen adsorption–desorption isotherms (Fig. 2a) typical of mesoporous solids (type IV of BDDT classification). However, the solid synthesised *via* Method 1 presents lower porous volume and pore diameter compared to the one obtained following Method 2 (Table 2, entries 3 and 4), while the loading stays unchanged. This is probably due to the presence of unreacted chlorinated arms when Method 1 is used. The correlation between the amount of incorporated macrocycles and the textural data for the solids obtained by Method 2 has been studied. The curves in Fig. 3 show that both the surface area (curve A) and the pore volume (curve B) decrease linearly with the increase of cyclam content. The advantages of Method 2, with respect to Method 1, are as follows: a much higher amount of grafted cyclam, no residual chlorine atoms and no

Table 2 Textural data for the different materials

Entry	Method of attachment	Material	Cyclam content/ mmol g^{-1}	^{29}Si NMR	S_{BET}/m^2 g^{-1}	Porous volume/ cm^3 g^{-1}	Mean pore diameter /Å
1	—	SiO_2	0	Q^2, Q^3(M), Q^4	415	0.77	60[a]
2	1	M1-Cl	0	—	372	0.52	47[a]
3	1	M1-Cyc	0.38	T^2, T^3, Q^3(M), Q^4	341	0.45	45[a]
4	2	M2-Cyc1	0.38	—	320	0.54	54[a]
5	2	M2-Cyc2	0.81	T^2, T^3, Q^3(M), Q^4	265	0.33	50[a]
6	3	M3-Cyc5	1.54	T^2, T^3, Q^2, Q^3(M), Q^4	350	0.21	20[b]
7	3	M3-Cyc10	0.97	T^2, T^3, Q^2, Q^3(M), Q^4	594	0.80	100[a]

[a]Only mesopores. [b]Both micro and mesopores.

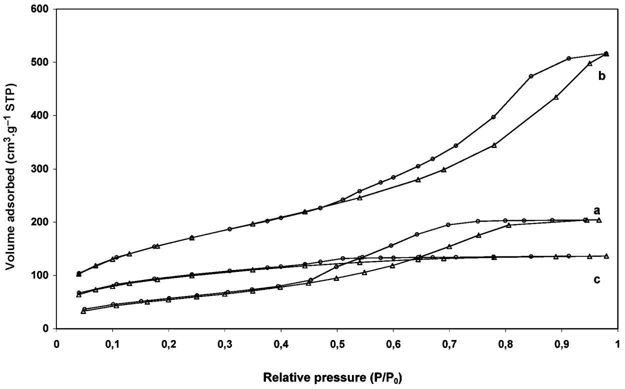

Fig. 2 N_2 adsorption (△)–desorption (○) isotherms for (a) M2-Cyc2, (b) M3-Cyc10 and (c) M3-Cyc5 after degassing for 2 h at 393 K.

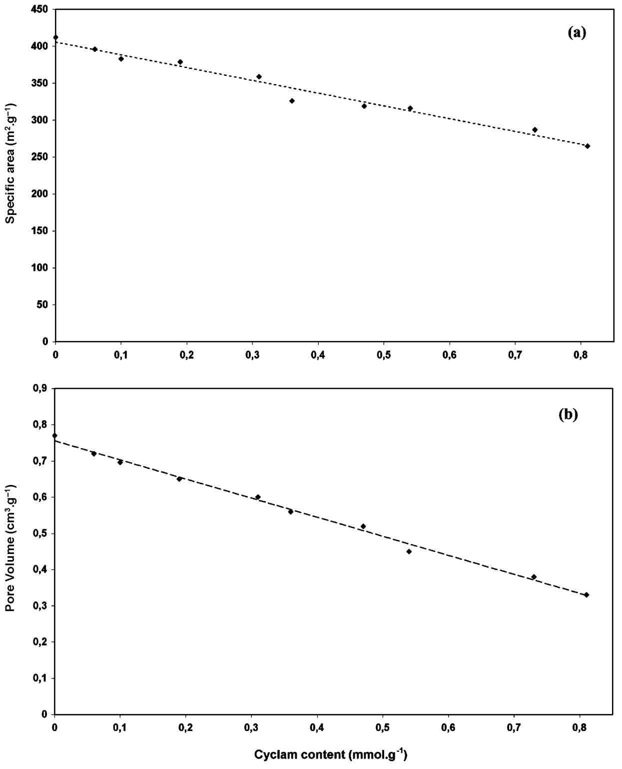

Fig. 3 Surface area (a) and pore volume (b) as a function of cyclam content.

Table 3 Metalation of different materials with $CuCl_2{\cdot}2H_2O$

Entry	Material	Cyclam content/ mmol g^{-1}	Copper content/ mmol g^{-1}	% of metalated sites
1	M1-Cyc	0.38	0.35	92
2	M2-Cyc2	0.81	0.75	93
3	M3-Cyc5	1.54	1.28	83
4	M3-Cyc10	0.97	0.97	100

polysubstitution. However, the textural properties of the materials prepared by both approaches are strongly dependent on those of the starting silica gel. The incorporation of the cyclam moiety during the formation of the inorganic network (Method 3) gives silica gels with different textures depending on the amount of TEOS used. Indeed, by using 5 equiv. of TEOS, the xerogel presents a mixed type I–type IV isotherm (Fig. 2c) representative of both micro- and meso-pores. The xerogel M3-Cyc10 is only mesoporous (Fig. 2b) and exhibits large specific area and porous volume (Table 2, entry 7). The solid M3-Cyc5 presents a very high cyclam content but a weak porous volume (Table 2, entry 6).

Copper uptake. Copper has been chosen as a probe in order to check that the chelating properties of the cyclam moieties were not affected by incorporating the macrocycle onto the silica gels. Copper uptake for all materials has been determined by X-ray fluorescence. It is worth noting that the silica itself does not retain copper in the metalation conditions (in methanol at room temperature), and after washing three times with methanol. Consequently, the values in Table 3 correspond to coordinated copper only. A large amount of cyclam moieties are metalated (up to 100% for M3-Cyc10), indicating a good accessibility of the macrocycles into the solid for all the materials. Such a result was predictable for M1-Cyc and M2-Cyc2 but it is interesting to note that the sol–gel process involved in Method 3 also yields materials with cyclam moieties located at the surface of the silica gel. The same behaviour has already been reported in the case of linear amines.[24]

Oxygenation

Cyclam incorporating materials have been metalated by cobalt(II) and the amount of cobalt has been determined by X-ray fluorescence. The values range from 0.28–0.32 mmol g^{-1} (Table 4) for materials incorporating 0.38 mmol g^{-1} of cyclam (entries 1–3), to 0.46 and 0.58 mmol g^{-1} for more loaded silica gels (entries 4 and 5), *i.e.* 50–85% of metalated sites.

ESR data. The lower field region of the spectrum indicates that $[Co(cyclam)]^{2+}$ immobilised on silica displays an axially symmetrical signal under inert atmosphere (Fig. 4a), typical of low spin Co(II) in a D_{4h} or C_{4v} symmetry ($g_\perp = g_x \approx g_y$), and in a $^2A_1$ ground state with the unpaired electron in the d_{z^2} orbital.[25] The ESR data (Table 5) of the low spin Co(II) spectrum is very close to those of planar [Co(porphyrin)],[26] [Co(phthalocyanine)][27] or $[Co(cyclam)]^{2+}$[28] in solution or intercalated in clays[29] or zeolites.[30] The perpendicular spectrum feature is characteristic of hexacoordinated[27] cobalt with two water molecules or two chloride axial ligands observed in the solid state. The magnitude of $A_\perp$ can be used to estimate the

Table 4 Thermodynamic data at 293 K for dioxygen and dinitrogen adsorption by cobalt-complexed materials

			O_2				N_2				
Entry	Compound	V_{O_2} adsorbed at 760 Torr $cm^3\ g^{-1}$	V_1 $cm^3\ g^{-1}$	$(P_{1/2})_1{}^a$ Torr	V_2 $cm^3\ g^{-1}$	$(P_{1/2})_2{}^a$ Torr	V_{N_2} $cm^3\ g^{-1}$	$(P_{1/2})_{N_2}{}^a$ Torr	[Cyc] mmol g^{-1}	[Co] mmol g^{-1}	% of active sites
1	M1-CycCoCl_2	1.06	0.17	8.90	2.27	1180	1.68	1190	0.38	0.31	2.4
2	M1-CycCo$(BF_4)_2$	1.46	0.33	3.68	2.40	880	1.51	750	0.38	0.32	4.6
3	M2-Cyc1CoCl_2	1.89	0.34	2.92	4.13	1240	2.94	1350	0.38	0.28	5.4
4	M2-Cyc2CoCl_2	3.00	1.34	1.91	6.20	2100	2.45	1290	0.73	0.58	10.3
5	M3-Cyc10CoCl_2	2.30	0.38	4.46	3.56	680	3.51	1010	0.95	0.46	3.5

[a] $(P_{1/2})_i = 1/K_i$.

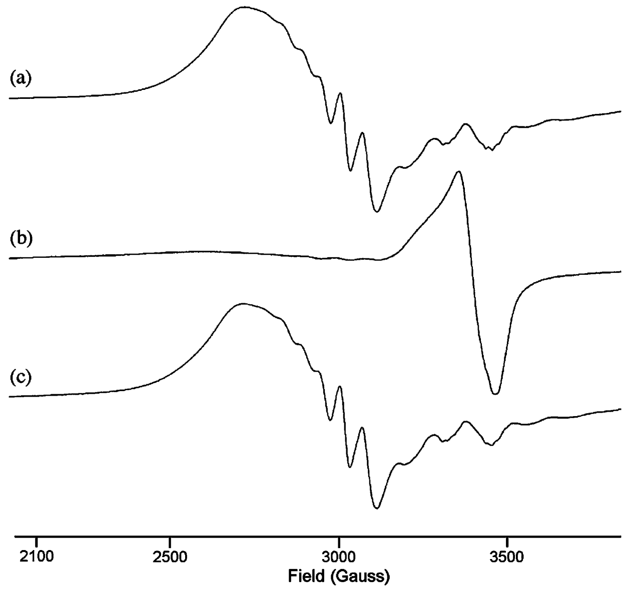

Fig. 4 ESR spectra at 100 K of M1-Cyc$CoCl_2$ (a) under argon, (b) after exposure to O_2 for 2 h at 293 K and (c) after degassing under 10^{-3} Torr for 1 h at 333 K.

strength of the axial coordination to Co(II) in a D_{4h} symmetry. The small difference between $A_\perp$ values for [Co(cyclam)-$(OH_2)_2]Cl_2$ in solution and for the metalated materials (Table 5) clearly indicates that the ligand field strength is nearly the same in all the cobalt complexes, while the higher value of $A_\perp$ observed for $[Co(cyclam)]^{2+}$ in zeolite Y is due to a different coordination number.[30] Thus, the incorporation of $[Co(cyclam)]^{2+}$ in silica does not affect the coordination scheme of the low spin $[Co(cyclam)]^{2+}$. The ESR data show that the coordination number and the coordination scheme are not affected by the anchoring method or the macrocycle content.

After exposure to 1 atm of dioxygen at 293 K, the original low-spin Co(II) spectrum is dramatically modified. The parallel part of the Co(II) spectrum is not observed due to its superposition with the characteristic superoxide[31,32] spectrum at $g \approx 2$ resulting from the oxygenation of the $[Co(cyclam)]^{2+}$. The signal at $g_\perp \approx 2.40$ of Co(II) decreases *versus* time while the $Co(O_2)$ radical species at $g = 2.04$ increases. The integration of the Co(II) perpendicular and the $Co(O_2)$ signals reveals that some Co(II) species are present even after oxygenation for several hours. This result shows that the oxygenation is not complete, as proved by the sorption measurements (*vide infra*), and demonstrates that all the cobalt atoms are not accessible or reactive towards dioxygen. Deoxygenation under vacuum (10^{-3} Torr) at 333 K for 1 h induces the total removal of chemisorbed dioxygen (Fig. 4c). The decreasing in intensity of the perpendicular spectrum of cobalt(II) (Fig. 4b) clearly indicates that the active cobalt species is in a low spin hexacoordinated configuration. This is in contrast with the high spin electronic state observed in zeolite Y[30] corresponding to a *cis*-configuration of $[Co(cyclam)]^{2+}$ which is ESR silent due to the short relaxation time of the $S = 3/2$ electronic state.

Dioxygen sorption. The reaction of dioxygen with $[Co(cyclam)]^{2+}$ grafted on silica is described by eqn. (1), where LCo^{2+} is the cobalt complex incorporated in the material and $LCo(O_2)$ is the corresponding oxygenated complex.

$$LCo^{2+} + O_2 \rightleftharpoons LCo(O_2) \quad K = \frac{[LCo(O_2)]}{[LCo^{2+}]\cdot P_{O_2}} \qquad (1)$$

The adsorption isotherms of dioxygen and dinitrogen for M2-Cyc$CoCl_2$ are represented in Fig. 5. The adsorption of dinitrogen is representative of physisorption of gas on the material and may be considered as a blank. Indeed, the isotherms obtained for the adsorption of dinitrogen are similar to those obtained for dioxygen adsorption using silica gels containing no metal or metal inactive towards dioxygen such as copper(II). The adsorption isotherm of dioxygen is the result of two different processes, the chemisorption of dioxygen on the cobalt complexes and the physisorption onto the silica matrix. The experimental isotherms have been analysed using a multiple adsorption process[33] based on the multiple-site Langmuir-type adsorption model. This model is required to adequately describe a chemical system with heterogeneous energetic interactions, such as a low energetic adsorption on

Table 5 ESR data at 100 K for cobalt and oxygenated adduct

	Co(II) complexes				$Co(O_2)$	
Compounds	$g_\parallel$	$A_\parallel/10^{-4}\ cm^{-1}$	$g_\perp$	$A_\perp/10^{-4}\ cm^{-1}$	$g_\parallel$	$A_\parallel/10^{-4}\ cm^{-1}$
$[Co(cyclam)(OH_2)_2]Cl_2{}^a$	2.04	104	2.38	52	2.03	25
M1-Cyc$CoCl_2$	2.04	114	2.41	70	2.08	25
M1-CycCo$(BF_4)_2$	2.04	122	2.38	73	2.08	[c]
M2-Cyc$CoCl_2$ [Cyc] = 0.38	2.04	110	2.40	66	2.08	[c]
M2-Cyc$CoCl_2$ [Cyc] = 0.73	2.03	115	2.40	68	2.08	[c]
M3-Cyc10$CoCl_2$	2.03	119	2.41	71	2.08	[c]
$[Co(cyclam)]^{2+}$-Y^b	1.95	150	2.70	200	—	—

[a] In methanolic frozen solution (100 K). [b] Reference 30. [c] Not measurable.

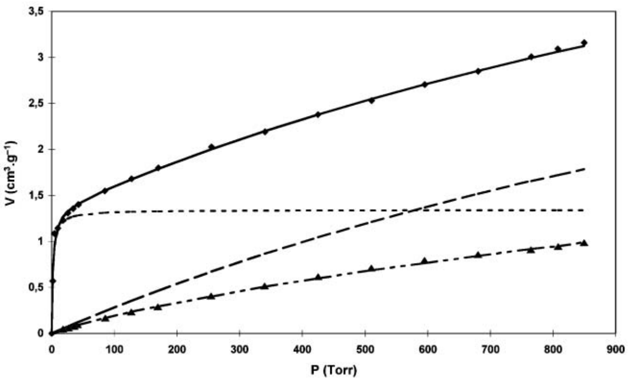

Fig. 5 Adsorption isotherm of O_2 and N_2 by M2-CycCoCl_2 ([Cyc] = 0.73 mmol g^{-1}) at 293 K, with ◆ experimental data for O_2, ▲ experimental data for N_2, — calculated isotherm for O_2, ··· component 1 of the isotherm, – – – component 2 of the isotherm, — - - calculated isotherm for N_2.

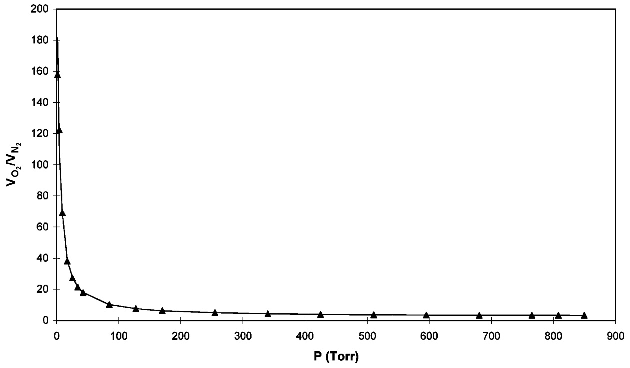

Fig. 6 Selectivity O_2/N_2 *versus* pressure for M2-CycCoCl_2 ([Cyc] = 0.73 mmol g^{-1}) at 293 K, ▲ experimental data, and — calculated selectivity.

porous silica materials (3–6 kcal mol^{-1}) and higher energetic interaction for dioxygen binding on cobalt complexes (10–18 kcal mol^{-1}).[14,32,34] The eqn. (2) has been used.

$$V = \frac{V_1 \cdot K_1 \cdot P}{1 + K_1 \cdot P} + \frac{V_2 \cdot K_2 \cdot P}{1 + K_2 \cdot P} \qquad (2)$$

V is the STP volume of dioxygen adsorbed at pressure P, process 1 (K_1 and V_1) corresponds to the chemisorption of dioxygen on the cobalt complexes, while process 2 (K_2 and V_2) relates the physisorption of dioxygen on the silica matrix. A similar model describing two sites with different adsorption energies was also required to describe the adsorption of isooctane on MFI zeolite.[35] Only one Langmuir equation was considered for dinitrogen binding. The V_i and K_i values were determined using a nonlinear least-squares minimisation algorithm. The calculated isotherm (Fig. 5) for dioxygen is the summation of the two processes, process 2 corresponding to weak interactions with the matrix leads to a straight line of Henry-type mode. Process 1 is predominant at lower pressures (< 50 Torr) due to the high affinity of the cyclam complex for dioxygen and process 2 is predominant for higher pressures.

The thermodynamic data presented in Table 4 clearly show that cyclam incorporating materials exhibit a great affinity towards dioxygen with $(P_{1/2})_1$ ($= 1/K_1$) varying from 1.9 to 8.9 Torr and a total V_{O_2} adsorbed at 760 Torr ranging from 1 to 3 cm^3 g^{-1}. However, it is noteworthy that the efficiency of the materials depends on several parameters. Thus, for the same loading, Method 2 yields a material presenting a higher percentage of active sites and a lower $(P_{1/2})_1$ value (Table 4, entries 1 and 3) while the presence of disubstituted cyclams in the materials obtained by Method 1 leads to a weaker adsorption. This result correlates with the study of the oxygenation in aqueous solution of cyclam and polyalkylated cyclams cobalt(II) complexes, the affinity of the metal complexes towards dioxygen decreasing while adding alkyl chains. Indeed, the decrease of equatorial ligand field strength gives a lower metalation constant with M(II) (M = transition metal)[36] and reduces the energy of the cobalt d_{z^2} orbital containing the unpaired electron. The $[Co(1,4,8,11\text{-tetramethylcyclam})]^{2+}$ is thus totally inactive towards dioxygen and the +II oxidation state of cobalt in a high spin state is the most stable oxidation state when coordinated to this ligand.[37]

Comparison of entries 3 and 4 (Table 4) corresponding to materials obtained by Method 2 shows that the concentrations of cobalt and cyclam grafted onto silica do not affect critically the affinity of the cobalt complex but influence the relative capacity (V_1) of the material. The more loaded M2-Cyc2CoCl_2 material (Table 4, entry 4) shows the highest activity towards dioxygen considering both the affinity $(P_{1/2})_1$ and the number of cobalt active sites. This result is probably due to a weak intermetallic cooperative effect due to the high cobalt concentration.

The material M3-CycCoCl_2 presents $(P_{1/2})_1$ and (V_1) average values with respect to its high loading (Table 4, entry 5). The low percentage of active sites observed is attributable to the lack of homogeneity of this cogel.

The effect of the counter-ion coordinated to the cobalt is shown while comparing entries 1 and 2 in Table 4. The higher capacity and affinity towards dioxygen of M1-CycCo$(BF_4)_2$ *versus* M1-CycCoCl_2 are undoubtedly attributed to the higher lability of the counter-anions which may dissociate before oxygenation of the hexacoordinated cobalt complex. The effect of various ligands coordinated to the metal is now under investigation.

The values K_2 and K_{N_2} are quite similar proving that interactions with the matrix are equivalent for O_2 and N_2. The materials show high selectivity for dioxygen over dinitrogen in a gas mixture, as illustrated in Fig. 6, V_{O_2}/V_{N_2} is greater than 100 for partial pressure below 5 Torr.

The reversibility of the oxygenation reaction, as shown qualitatively by ESR, has been studied and the active species appeared to be stable after 3 adsorption/desorption cycles at 120 °C for 2 h under 10^{-3} Torr. Even the most loaded material presents a high reversibility. However, due to the high value of K_1, the process is not reversible when desorption occurs at 20 °C.

The adsorption measurements and ESR results clearly show that oxygenation proceeds almost exclusively *via* the formation of a mononuclear cobalt superoxide adduct, and that the dioxygen species is more stable and reversible in the solid state than in aqueous solution.[16]

The concentration of active cobalt atoms (V_1/theoretical volume ratio) ranges from 2.4 to 10.3%. The percentage of active sites might be compared to the values reported in the case of cobalt(II) cyanide,[7] cobalt(II) Schiff bases,[10–13] Co(bpy)(tpy)$^{2+}$ [9] and $[Co(cyclam)]^{2+}$ [30] complexes inside zeolite Y, but the total concentration of active sites is higher due to the high loadings in the cyclam incorporating silica gels. To our knowledge, the cobalt tetramethylporphine (Co(tmp)) complex in zeolite Y is the species where the highest number of active sites is observed but is characterised by a low affinity towards dioxygen (Table 6). The adsorption properties of $[Co(cyclam)]^{2+}$ grafted on silica show that these materials range among the best dioxygen binding materials at room temperature considering both the high affinity and the high concentration of active sites. These materials lead mainly to a 1 : 1 superoxo mononuclear species, characterised by ESR, rather similar to $[Co(cyclam)]^{2+}$ inside zeolite Y[30] and the high reactivity of these systems is due to the high ligand field strength of the macrocycle. Moreover, the cyclam incorporating materials are almost the only ones capable of coordinating

Table 6 $(P_{1/2})_{O_2}$ and V_{O_2} adsorbed values for materials incorporating cobalt complexes

Compound	$(P_{1/2})_{O2}$ at 293 K (Torr)	V_{O_2} adsorbed at 760 Torr/cm^3 g^{-1} (% of active sites)	Reference
M2-CycCoCl$_2$ [Cyc] = 0.73	1.9	3.0 (10.3)	This work
Co(tmp)-Y	105	29 (100)	[14]
Co(CN)$_x$-Y	9	0.2 (1)	[6]
Co(salen)Py^{2+}-Y	306	—	[10]
Co(smdpt)$^{2+}$-Y	12	0.4 (11)	[11]
Co(bpy)(terpy)$^{2+}$-Y	0.6	0.4 (8)	[8]
[Co(cyclam)]$^{2+}$-Y	$\leqslant$ 0.75	2.2 (15)	[30]

dioxygen without adding an exogenous or endogenous axial base such as pyridine or imidazole,[34,38] apart from some cyanocobaltates[39] and porphyrin[14] complexes.

Conclusion

Three different routes have been described for the synthesis of cyclam containing silica gels. The use of a monosilylated cyclam as precursor yields the most efficient porous materials, both in terms of macrocycle contents, metal concentration, or high affinity of cobalt complexes towards dioxygen. Some of the solids obtained show behaviours among the best dioxygen binding systems. Indeed, they display a good compromise between a high affinity implying a strong of selectivity for dioxygen over dinitrogen and a reasonable volume of dioxygen adsorbed.

Experimental

Chemicals

Cyclam was synthesised in our laboratory.[40] The commercial silica gel used was Kieselgel 60 (bead size 0.2–0.5 mm, E. Merck). Sodium iodide and sodium carbonate were dried under vacuum (100 °C/1 Torr, 24 h). Acetone was dried and distilled over 4 Å molecular sieves. Methanol used for metalation with cobalt(II) was distilled under argon on $Mg(OCH_3)_2$ and stored on 3 Å molecular sieves. All other commercial reagents (Acros or Aldrich) were used as received without further purification.

Instrumentation

The solution ^{1}H, ^{13}C and ^{29}Si NMR spectra were recorded on a Bruker AC 200 at the Centre de Spectroscopie Moléculaire de l'Université de Bourgogne. Chemical shifts are referenced to $CHCl_3$ at $\delta = 7.24$ and $\delta = 77.4$ for ^{1}H and ^{13}C NMR spectra, respectively. The solid state CP/MAS ^{29}Si NMR spectra were recorded on a Bruker FTAM 300. The ESR spectra were recorded in the solid state on a Bruker ESP 300 spectrometer at X-band (9.6 GHz), from the Centre de Spectrométrie Moléculaire de l'Université de Bourgogne, equipped with a double cavity and a liquid nitrogen cooling accessory. The magnetic field was calibrated with DPPH as external standard ($g = 2.0036$). Sensitive dioxygen coumpounds were transferred in the ESR tube in a glove box under argon. The X-ray fluorescence measurements were performed on an Oxford Lab-X 3000 and Microanalyses by the Service Central d'Analyse du Centre National de la Recherche Scientifique, Vernaison, France. Surface area and pore volumes were measured with N_2 adsorption at 77 K using a Micromeritics ASAP 2010 analyser equipped with 1, 10 and 1000 Torr transducers, and employing a 48-point pressure table in adsorption/desorption ranging from 5 to 760 Torr for each sample degassed for 2 h at 393 K under a 10^{-3} Torr vacuum. Surface areas were obtained using a five-point BET calculation[41] and mesopore volumes were determined using the BJH method.[42] Gaseous uptake measurements at 293 K on [Co(cyclam)]$^{2+}$ incorporating silica were performed on the same apparatus employing a 20-point pressure table ranging from 1 to 850 Torr. The experimental isotherms were interpreted using eqn. (2). The thermodynamic values were calculated from the experimental data using the Microsoft Excel 98 program using a nonlinear regression least-squares method with a conjugate-gradient or Newton algorithm.

Silica immobilised cyclams

Method 1. This procedure is a slight modification of the method previously described.[3] First the silica gel Kieselgel 60 (5.0 g) was refluxed in xylene (50 ml) until no more water was removed by azeotropic distillation using a Dean–Stark apparatus. Then (3-chloropropyl)triethoxysilane (3.0 g, 0.0125 mol) was added and the suspension was refluxed under mechanical stirring for 24 h. The solid was filtered off and washed with xylene, acetone and finally diethyl ether. A mixture of this modified silica gel and 1 g (5 mmol) of cyclam was mechanically stirred for 24 h in refluxing xylene (100 ml). The new silica gel was filtered off, washed with water until no pink or purple colour was detected when $CuSO_4$ was added to the filtrate (evidence of the presence of excess cyclam), hot methanol and diethyl ether. CP/MAS ^{29}Si NMR: −61 (T^2), −68 (T^3), −101 (Q^3), −111 (Q^4).

Method 2. *Synthesis of iodopropyltriethoxysilane.* Sodium iodide (36.5 g, 0.243 mol) was dissolved in 150 ml of acetone and chloropropyltriethoxysilane (58.6 g, 0.243 mol) was added dropwise. The mixture was then stirred under reflux for 24 h under an argon atmosphere. The white precipitate formed (NaCl) was filtered and the filtrate was concentrated. The crude compound was distilled (bp: 120–125 °C/1 Torr) and pure iodopropyltriethoxysilane was obtained as a pale yellow liquid (46.6 g, 58%). ^{1}H NMR (200 MHz, $CDCl_3$): 0.70 (m, 2 H), 1.20 (t, 9 H), 1.91 (m, 2 H), 3.19 (t, 2 H), 3.80 (q, 6 H). ^{13}C NMR (50 MHz, $CDCl_3$): 11.1, 13.1, 19.0, 28.4, 59.2.

Synthesis of 1-[(3-triethoxysilyl)propyl]-1,4,8,11-tetraazacyclotetradecane. A suspension of cyclam (72 g, 0.359 mol) and anhydrous sodium carbonate (15 g, 0.142 mol) in 2.5 l of acetonitrile was refluxed and a solution of iodopropyltriethoxysilane (24.2 g, 0.073 mol) in 500 ml of acetonitrile was added dropwise. The mixture was stirred under reflux for 48 h under an argon atmosphere. After evaporation of the solvent, pentane was added and excess cyclam was filtered. This work up was repeated three times until no precipitate appeared by adding pentane. The filtrate was concentrated to give the title compound as a colorless oil (28 g, 95%). ^{1}H NMR (200 MHz, $CDCl_3$): 0.46 (m, 2 H), 1.10 (t, 9 H), 1.43 (m, 2 H), 1.59 (m, 4 H), 2.30–2.70 (m, 18 H), 3.69 (q, 6 H). ^{13}C NMR (50 MHz, $CDCl_3$): 8.6, 18.9, 26.9, 29.6, 48.4, 48.7, 49.6, 50.0, 50.1, 51.6, 53.9, 55.2, 56.1, 58.9. ^{29}Si NMR (39.7 MHz, $CDCl_3$): −44.8. $C_{19}H_{44}N_4O_3Si$ (404.3): calc. C 56.4, H 11.0, N 13.9; found C 56.1, H 11.0, N 12.8%.

Grafting onto silica gel. Silica gel Kieselgel 60 (5.0 g) was dried as described above in xylene (50 cm^3). Then 1-[(3-triethoxysilyl)propyl]-1,4,8,11-tetraazacyclotetradecane was added in different concentrations ranging from 0.082 to 2.5 mmol per 1 g of silica gel. The suspension was refluxed under mechanical stirring for 96 h. The new silica gel was filtered off, washed with xylene, water until no pink or purple colour was detected when $CuSO_4$ was added to the filtrate, acetone and finally diethyl ether. CP/MAS ^{29}Si NMR: −61 (T^2), −68 (T^3), −101 (Q^3), −111 (Q^4).

Method 3. *M3-Cyc5.* 1-[(3-triethoxysilyl)propyl]-1,4,8,11-tetraazacyclotetradecane (2.0 g, 4.95 mmol) and tetraethoxysilane (5.14 g, 24.67 mmol) were dissolved in 29 ml of ethanol in a 100 ml vial. 1 ml of water and 2.9 ml of a 0.1 M TBAF solution in ethanol were added to the solution. At 20 °C, the gelation time was less than 35 min. The xerogel was allowed to age for 5 days at room temperature before being powdered, washed three times with ethanol and diethyl ether and finally dried (120 °C at 20 Torr for 12 h) to afford 2.79 g of M3-Cyc5 as a white powder. CP/MAS ^{29}Si NMR: −63 (T^2), −66 (T^3), −94 (Q^2), −102 (Q^3), −107 (Q^4).

M3-Cyc10. A similar procedure was used to synthesize M3-Cyc10, starting from 1.9 g (4.70 mmol) of 1-[(3-triethoxysilyl)-propyl]-1,4,8,11-tetraazacyclotetradecane, 9.78 g (46.94 mmol) of tetraethoxysilane, 52 ml of ethanol, 1.82 ml of water and 5.17 ml of a 0.1 M TBAF solution in ethanol. At 20 °C, the gelation time was less than 15 min. The xerogel was allowed to age for 5 days at room temperature before being treated as described above to afford 4.28 g of M3-Cyc10 as a white powder. CP/MAS ^{29}Si NMR: −63 (T^2), −66 (T^3), −94 (Q^2), −102 (Q^3), −107 (Q^4).

Metalation of cyclam incorporating silica

Copper(II) complexes were prepared by addition of a two-fold excess of copper(II) chloride dihydrate to a methanolic suspension of the xerogel or modified silica gel (0.5–1 g). The mixture was then allowed to equilibrate for 30 min, after which the material was filtered off under argon, washed several times with methanol and dried under vacuum.

Cobalt(II) complexes were prepared under argon using Schlenk techniques by addition of a two-fold excess of $CoCl_2 \cdot 6H_2O$ or $Co(BF_4)_2 \cdot 6H_2O$ to a methanolic suspension of the xerogel or the modified silica gel (0.3–0.5 g). The mixture was refluxed for 2 h then filtered off, washed several times with methanol and dried under vacuum.

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