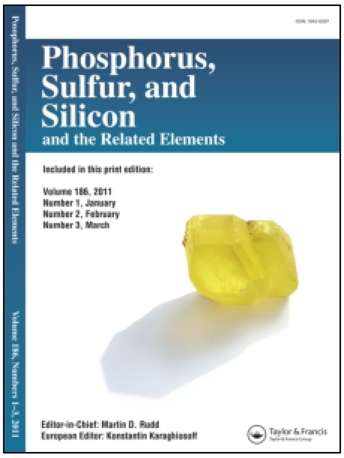
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Silica Gel Bound Cyclam. Synthesis and Applications

Franck Denat; Géraud Dubois; Raphaël Tripier; Stéphane Brandes; Roger Guilard

To cite this Article Denat, Franck , Dubois, Géraud , Tripier, Raphaël , Brandes, Stéphane and Guilard, Roger(2001) 'Silica Gel Bound Cyclam. Synthesis and Applications', Phosphorus, Sulfur, and Silicon and the Related Elements, 168: 1, 151 — 156

To link to this Article: DOI: 10.1080/10426500108546546

URL: http://dx.doi.org/10.1080/10426500108546546

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus Sulfur and Silicon, 2001, Vol. 168, pp. 151-156
Reprints available directly from the publisher
Photocopying permitted by license only

Silica Gel Bound Cyclam. Synthesis and Applications

FRANCK DENAT, GÉRAUD DUBOIS, RAPHAËL TRIPIER,
STÉPHANE BRANDES and ROGER GUILARD

*Laboratoire d'Ingénierie Moléculaire pour la Séparation et les Applications des Gaz, LIMSAG, UMR 5633, Faculté des Sciences Gabriel, 6, Bd Gabriel,
21100 DIJON – France*

Several silica gels containing cyclam have been synthesized using three different methods. The first two methods imply the modification of a commercial silica gel while the latter involves a sol-gel approach. The macrocycle contents and the textural data of these materials are compared. The efficiency of $[Co(cyclam)]^{2+}$ grafted onto silica for binding dioxygen is reported. Finally, N-functionalization of the macrocycle has been performed. Such modified silica gels might behave as highly selective ions exchangers.

Keywords: Silica gel; Cyclam; Cobalt complex; Dioxygen; N-functionalization

INTRODUCTION

Cyclic polyamines have long been known to form stable complexes with various guests[1]. 1,4,8,11-tetraazacyclotetradecane or cyclam and its N-functionalized derivatives have been some of the most extensively studied polyazacycloalcanes. These compounds show a great affinity towards transition metal cations but also main group elements. The presence of four secondary amine functions allows for a total or partial N-functionalization of the cyclam. Numerous works have been devoted to the regioselective functionalization of tetraazacycloalkanes[2]. A fine tuning of the coordinating properties of the ligand is made possible by varying the nature, the number and the relative positions of the appended arms. The selectivity towards a given guest can thus be strongly enhanced. N-Substitution of the macrocycle with convenient protecting groups is a route towards tridimensional molecules such as cyclam based cryptands or macrotricycles. Finally, introduction of a suitable arm on one of the four nitrogen atoms may allow for the anchoring of the cyclam on a antibody or onto a solid matrix.

These compounds find applications in various domains including waste water treatment, catalysis, and many medical purposes such as radioimmunotherapy or magnetic imaging. Some cyclam complexes exhibit a great affinity towards certain gases. Thus, cobalt complex of cyclam binds dioxygen to give a 1:1 superoxo species which may dimerize to form a μ-peroxo adduct. This oxygenated cobalt complex is hydrolyzed in solution leading to an irreversible oxidation of the metallic center. The Co(III) complex thus formed does not present anymore affinity towards dioxygen. One way to overcome the degradation of the oxygenated cobalt complex is to immobilize the active species on a solid matrix. Such approach provides favorable conditions for reversible addition of dioxygen, by decreasing the rate of the metal oxidation and preventing the formation of the μ-peroxo complex. The handling of the active species is also easier once it has been immobilized on a support.

In the field of waste water treatment, the immobilization of the macrocycle on a solid support represents undoubtedly a real advantage since such modified materials might be used in solid-liquid extraction processes. Cyclic polyamines are often soluble in both water and organic solvents and their immobilization prevents the lost of the ligand in solution.

Silica gel is a good candidate for all these applications since this porous material is a low cost material, mechanically and chemically stable and easily modifiable.

RESULTS

We have developed three different routes for the synthesis of cyclam bound silica gels (FIGURE 1). In the method 1, previously described[3], 3-chloropropyltriethoxysilane and a commercial silica gel are reacting in refluxing xylene. Cyclam is then added to this modified silica gel M1-Cl in xylene and the suspension is heated under reflux. The cyclam grafted silica gel M1-Cyc is thus obtained. The methods 2 and 3 which have been recently patented involve the use of a monosilylated cyclam[4]. The mono-N-functionalization of cyclam is performed following conventional procedure, by reacting an excess of cyclam (5 eq.) with iodopropyltriethoxysilane in refluxing acetonitrile in presence of potassium carbonate. Such conditions prevent the formation of di-, tri- or tetra-N-substituted macrocycles. The monosilylated cyclam thus obtained in 95 % yield may either react with a commercial silica gel, yielding the material M2-Cyc, or co-gelified with tetraethoxysilane (TEOS) to give M3-Cyc5 and M3-Cyc10 depending on the amount of TEOS. The hydrolysis of the mixture monosilylated cyclam / TEOS is performed by using a stoichiometric amount of water in the presence of 1% TBAF as a catalyst. The gelification occurs after a few minutes.

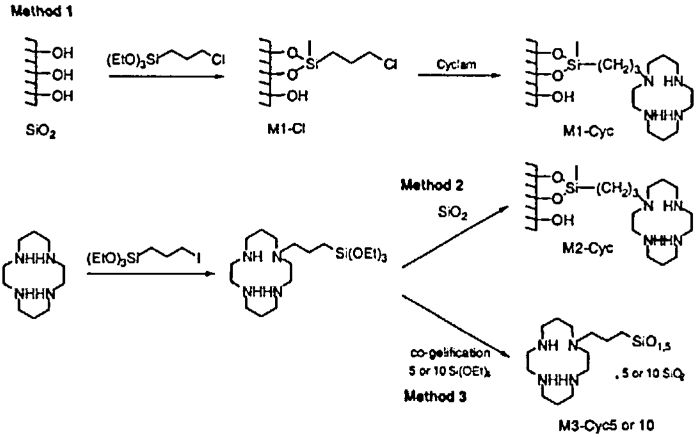


FIGURE 1 Synthesis of cyclam grafted silica gels.

The materials obtained have been characterized using many different methods. Specific areas and porosity have been determined by classical methods involving N_2 adsorption-desorption measurements. CP/MAS ^{29}Si NMR spectra revealed the grafting on silica gel by the apparition of T substructures. Cyclam content has been calculated from the nitrogen elemental analysis. Metal uptake capacities (copper and cobalt) might be obtained using spectroscopic methods such as ESR or X-ray fluorescence. Finally, the efficiency of $[Co(cyclam)]^{2+}$ grafted onto silica for binding dioxygen has been evaluated using ESR spectroscopy and static volumetric gas uptake measurements. The results are reported in TABLE 1 and TABLE 2.

Method of Attachment	Material	Chlorine content (mmol.g^{-1})	Cyclam content (mmol.g^{-1})	S_{BET} (m^2.g^{-1})	Porous Volume (cm^3.g^{-1})	Mean pore Diameter/Å
-	SiO_2	-	0	415	0.77	60^a
1	M1-Cl	1.08	0	372	0.52	47^a
1	M1-Cyc	0.38	0.38	341	0.45	45^a
2	M2-Cyc1	-	0.38	320	0.54	54^a
2	M2-Cyc2	-	0.81	265	0.33	50^a
3	M3-Cyc5	-	1.54	350	0.21	20^b
3	M3-Cyc10	-	0.97	594	0.80	100^a

[a] only mesopores
[b] both micro and mesopores

TABLE 1 Cyclam contents and textural data for the different materials.

The cyclam content depends on the method used. Indeed, more than 1.5 mmol of cyclam can be immobilized on 1 g of silica gel (about 30 w/w) following the sol-gel procedure. The macrocycle content in the materials synthesized by the method 2 increases linearly with the amount of monosilylated until 0.70 mmol.g^{-1}. Values up to 0.81 mmol.g^{-1} can be obtained by using a large excess of precursor. The material M1-Cyc is the less loaded silica gel and elemental analysis shows the presence of residual chlorine. It is noteworthy that the amount of grafted cyclam is less important than the difference between the chlorine contents before and after cyclam attachment, showing that some cyclam moieties are linked by more than one nitrogen atom.

Material	V_{O_2} adsorbed at 760 Torr (cm^3.g^{-1})	$(P_{1/2})_{O_2}$ at 293 K (Torr)	Cyclam content (mmol.g^{-1})	[Co] (mmol.g^{-1})	% of active sites
M1-CycCoCl$_2$	1.06	8.90	0.38	0.31	2.4
M2-CycCoCl$_2$	1.89	2.92	0.38	0.28	5.4
M2-CycCoCl$_2$	3.00	1.91	0.73	0.58	10.3
M3Cyc10 CoCl$_2$	2.30	4.46	0.95	0.46	3.5
[Co(cyclam)]$^{2+}$-Y	≤0.75	2.2	-	-	15
Co(tmp)-Y	29	105	-	-	100

$$LCo^{2+} + O_2 \xrightleftharpoons{K_{O_2}} LCo^{3+}\text{---}{}^{\cdot}O\text{-}O^{\cdot} \qquad (P_{1/2})_{O_2} = 1/K_{O_2}$$

TABLE 2 Fixation of O_2 by $[Co(cyclam)]^{2+}$ grafted silica gels.

The textural data of materials obtained by method 1 and 2 are strongly dependent on the texture of the starting silica gel. All these materials display N_2 adsorption-desorption isotherms typical of mesoporous solids. A common feature is a decrease of both the surface area and the porosity values while modifying the silica gel. Materials obtained by the sol-gel procedure show different textural data depending on the amount of TEOS used. Thus, the xerogel M3-Cyc5 contains both micro- and meso-pores while the less loaded M3-Cyc10 is only mesoporous.

The metalation of cyclam occurs in good yields since 50 to 90 % of the macrocycles are metalated by Co(II), depending on the material. It appears that the most cyclam loaded materials do not necessarily present the highest metal uptake. These $[Co(cyclam)]^{2+}$ grafted silica gels show a good affinity towards dioxygen. The material presenting both the best affinity (lowest $(P_{1/2})_{O_2}$) and the highest V_{O_2} adsorbed is the silica gel synthesized by the method 2 containing 0.73 mmol of cyclam per gram of silica. Compared to the same complex incorporated inside zeolite Y[5], the modified silica gel exhibits a better efficiency. The cobalt tetramethylporphine complex in zeolite (Co(tmp)-Y) is able to adsorb a higher volume of O_2 but the affinity is much lower[6]. The active species is stable after three cycles adsorption / desorption, showing a good reversibility of the system. Also the affinity towards O_2 is good enough to bring to these materials a great selectivity for dioxygen over nitrogen in a gas mixture.

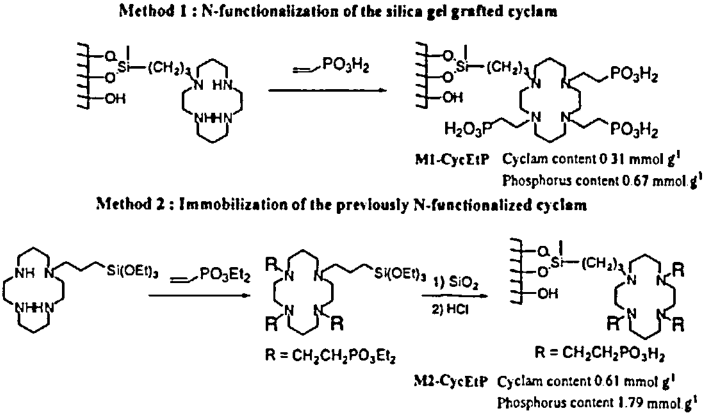


FIGURE 2 Immobilization of the silica gel grafted cyclam.

The N-functionalization of cyclam grafted on silica gel with carboxylic acid groups yields selective ion exchangers which have been successfully used for the ultimate decontamination of nuclear wastes[7]. We show in FIGURE 3 that the N-functionalization might be performed prior to the anchoring of the macrocycle. This method 2 involves the N-functionalization of the monosilylated cyclam previously described. Phosphonic acid groups have been chosen here in order to determine the number of N-substituents introduced from phosphorus elemental analysis. It appears clearly that the method 2, although more synthetically demanding, allows for a better control of the nature of the grafted macrocycle. Indeed, the cyclam is fully N-functionalized (N-substitution rate = 98 %) while the N-functionalization occurs in only 72 % when it is performed in the final step (Method 1).

CONCLUSION

The new methods described herein allow for the synthesis of high cyclam loaded materials. The texture of the final materials might be controlled either by the choice of the commercial silica gel (method 1) or by the amount of TEOS and the gelification conditions (method 2). We show that N-functionalization of the macrocycle might be performed in a quasi quantitative manner. Cobalt complexes of such modified silica gel exhibit a good affinity towards dioxygen while convenient N-functionalization may lead to highly selective ion exchangers.

References

[1] See for example R. M. Izatt, K. Pawlak, J. S. Bradshaw and R. L. Bruening, *Chem. Rev.*, 95, 2529–2586 (1995).

[2] F. Denat, S. Brandès and R. Guilard, *Synlett*, 561–574 (2000).

[3] C. Gros, F. Rabiet, F. Denat, S. Brandès, H. Chollet and R. Guilard, *J. Chem. Soc. Dalton Trans.*, 1209–1214 (1996).

[4] A. Mehdi, F. Denat, F. Barbette, R. Guilard and G. Lagrange, WO 9937399 (1999).

[5] D. E. De Vos, D. L. Vanoppen, X. Y. Li, S. Libbrecht, Y. Bruynseraede, P. P. Knops-Gerrits and P. A. Jacobs, *Angew. Chem., Int. Ed. Engl.*, 34, 144–149 (1995).

[6] G. Q. Li and R. Govind, *Inorg. Chim. Acta*, 217, 135–140 (1994).

[7] R. Guilard, H. Chollet, P. Guiberteau and P. Cocolios, WO 9629363 (1996).