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New silica-gel-bound polyazacycloalkanes and characterization of their copper(II) complexes using electron spin resonance spectroscopy

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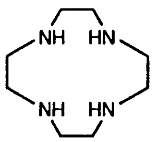
Several tetraazamacrocycle-bonded silica gels have been synthesized and characterized. 1,4,7,10-Tetraazacyclododecane, 1,4,8,11-tetraazacyclotetradecane and 1,5,9,13-tetraazacyclohexadecane have been covalently bound to silica gel and their respective copper(II) complexes characterized. Three different methods were used for capacity determinations: quantitative ESR measurements of copper(II) complexes, nitrogen, carbon and copper elemental analysis and UV/VIS measurements.

The high selectivity and strong co-ordination of polyazacycloalkanes with transition-metal ions have been well established and make these compounds ideal candidates for use in metal-ion separations. In the past, polyazacycloalkanes have been employed in aqueous environments with membrane systems or solvent extractions. These systems exhibit high selectivity resulting in cation extraction, but one of the major problems is the solubility of the ligand in water or organic phases. This makes their commercial use expensive, difficult to monitor and environmentally hazardous. One way to overcome these problems is by covalent bonding of the macrocycles to a solid support, thereby greatly enhancing their usefulness. Indeed, during the last decades, many studies have focused on the surface modification of various supports in fields as diverse as dioxygen transport,[1,2] waste-water treatment,[3–6] metal-ion chromatography[7,8] or recovery of trace-metal ions.[9–12] The solid support can be selected from synthetic organic polymers, natural polymers such as cellulose or inorganic materials such as alumina or silica gel. Silica gel has been used in most applications. Indeed, macrocycles are attached to silica gel *via* relatively simple reactions, especially when compared with immobilizations involving organic polymers. Moreover, silica gel is a low-cost starting material which exhibits good mechanical strength and swelling, required for use in high-performance liquid chromatography systems. For example, macrocycles have been attached to silica gel by amide linkages[9] and by covalent carbon–silane bonds through a hydrosilylation process.[13]

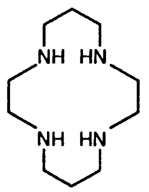
Our major interest in this field is the production of modified silica gel as a polymeric support for both waste-water treatment and for purification of gases containing small amounts of dioxygen contamination. We report here three ways to graft tetraazacycloalkanes onto silica gel, and also a new ESR quantification method for their corresponding copper(II) complexes. As in the literature the metal uptake is, in most cases, measured by back titration and little attention, if any, has been given to whether or not the macrocycle sites are totally metallated. A direct ESR quantification technique is therefore presented.

Experimental

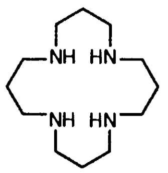
Chemicals



1,4,7,10-tetraazacyclododecane, L^1 (cyclen)



1,4,8,11-tetraazacyclotetradecane, L^2 (cyclam)



1,5,9,13-tetraazacyclohexadecane L^3

Macrocycles were synthesized in our laboratory.[14] Two silica gel supports (from two batches) were used: Kieselgel 60 (bead size 0.2–0.5 mm, specific area 550 m^2 g^{-1}, E. Merck) and 3-aminopropyl-functionalized silica gel (Aldrich). The silanes (3-chloropropyl)triethoxysilane and [3-(2,3-epoxypropyloxy)-propyl]trimethoxysilane were employed. Purified water (18 MΩ) obtained with an Elgastat UHQ II apparatus was used for preparing all water solutions. All other reagents were analytical grade used as received. The parent tetraazamacrocycles were as illustrated above.

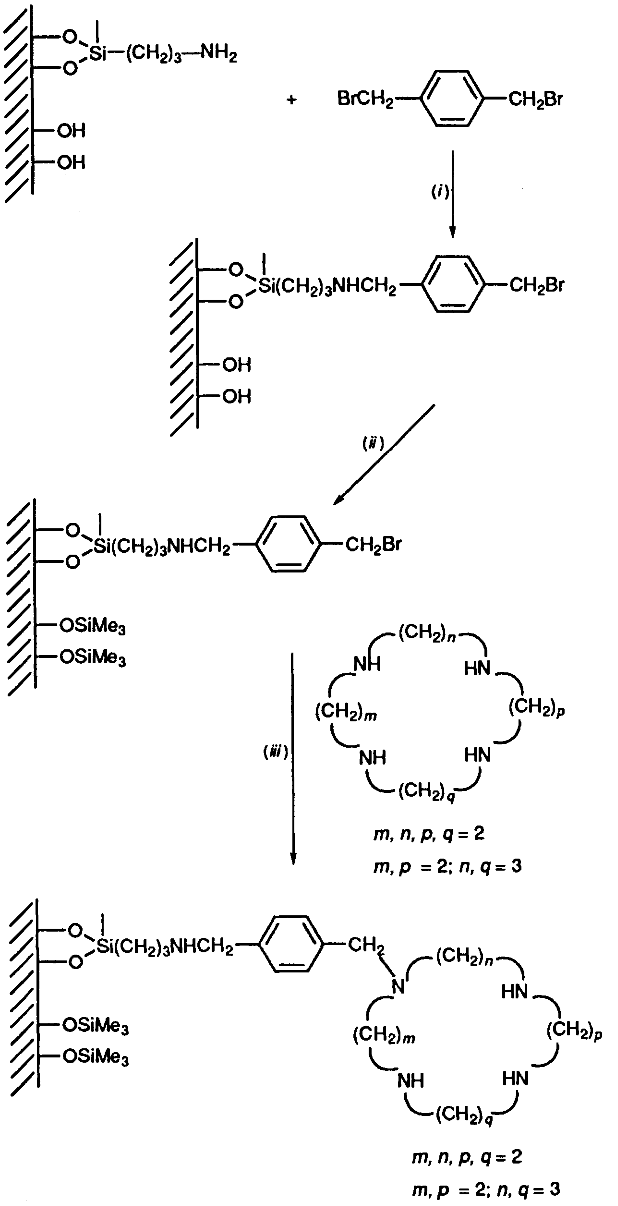
Instrumentation

The ESR spectra were recorded in the solid state on a Bruker ESP 300 spectrometer situated at the Centre de Spectroscopie Moléculaire de l'Université de Bourgogne, UV/VIS spectra on a Varian Cary 1 spectrophotometer. Microanalyses were performed by the Service Central d'Analyse du Centre National de la Recherche Scientifique, Vernaison, France.

Preparation of functionalized silica gels

Method 1. A new versatile preparation of modified silica gel was developed, and proceeds in three steps as described in Scheme 1. First, 3-aminopropyl-functionalized silica gel (Aldrich) (2.0 g) and α,α'-dibromo-*p*-xylene (1.0 g) were refluxed under argon for 24 h in dried acetonitrile (30 cm^3) and triethylamine (0.5 cm^3). The resulting modified silica gel was then filtered off, washed thoroughly with CH$_2$Cl$_2$ (250 cm^3) and dried over 24 h under high vacuum (yield 2.6 g).

End-capping of unreacted silanol groups. The end-capping was done as previously described by Félix and Bertrand.[15] A suspension of silylated silica gel (2.6 g) in SiMe$_3$Cl (30 cm^3) was refluxed for 4 h under argon. The modified silica gel was filtered off and washed several times successively with toluene



Scheme 1 (*i*) MeCN, NEt_3, reflux, 24 h; (*ii*) $SiMe_3Cl$, reflux, 4 h; (*iii*) toluene, NEt_3, reflux, 48 h

($100 cm^3$), tetrahydrofuran ($100 cm^3$) and dichloromethane ($100 cm^3$). The product was then dried under vacuum for 24 h (yield 3.1 g).

Polyazacycloalkane attachment. A solution of polyazamacrocycle (cyclen, cyclam; 1.0 g) in toluene ($50 cm^3$) was added to the modified silica gel (2.0 g) and the mixture refluxed for 48 h under argon with triethylamine ($0.5 cm^3$). The mixture was then filtered off and the silica gel washed successively with water ($200 cm^3$), dilute hydrochloric acid ($200 cm^3$), water ($200 cm^3$, to remove traces of HCl) and hot methanol ($200 cm^3$). The material was then dried for 24 h under high vacuum (yield 1.6 g).

Method 2. The first step (Scheme 2) was a slight modification of the procedure described by Burwell and co-workers.[2]

Silylation reaction. First, silica gel (Merck) (5.0 g) was dried at 120 °C under reduced pressure (10^{-3} mbar, 0.1 Pa) for 12 h and then refluxed in xylene ($50 cm^3$) under argon for 24 h with (3-chloropropyl)triethoxysilane (3.0 g). The modified silica was then filtered off and washed several times with dry toluene ($100 cm^3$), acetone ($100 cm^3$) and diethyl ether ($100 cm^3$) (yield 5.8 g).

End-capping of unreacted silanol groups. The end-capping was done as previously described by Lindoy and co-workers.[9] with slight modification. A suspension of the above silylated silica gel (in about 3 or 4 times its weight of chlorotrimethylsilane) was refluxed for 4 h under argon. The excess of reactant was removed under vacuum and the modified silica gel washed with distilled water to neutral pH. The product was then dried under vacuum for 12 h (yield 6.5 g).

Polyazacycloalkane attachments. A solution of polyazacycloalkane (1.0 g) in xylene ($100 cm^3$) was added to the modified silica gel (5.0 g) and the mixture sonicated for 15 min. The suspension was then refluxed for 24 h without stirring. Occasionally, the mixture was gently stirred or carefully shaken to prevent damage to the particles. The excess of macrocycle was filtered off and the support washed with dilute hydrochloric acid ($0.1 mol dm^{-3}$) and water (until no pink or purple colour was detected when $CuSO_4$ was added to the filtrate) and finally with hot methanol (yield 4.8 g).

Method 3. The third procedure is outlined in Scheme 3. The first and third steps, described previously by Bagnoud *et al.*[16] in the case of cyclam, have been extended to the attachment of other tetraazamacrocycles and, in addition, the end-capping of the unreacted silanol groups has been accomplished.

Silylation reaction. First, silica gel (Merck) (5.0 g) was dried at 120 °C under reduced pressure (10^{-3} mbar) for 12 h before use. Dry toluene ($70 cm^3$), [3-(2,3-epoxypropyloxy)propyl]trimethoxysilane ($7 cm^3$) and triethylamine (150 μl) were then added and the mixture was refluxed under nitrogen for 4 h. The modified silica gel was then filtered off and washed several times with dry toluene ($100 cm^3$), acetone ($100 cm^3$) and ether ($100 cm^3$) (yield 6.1 g).

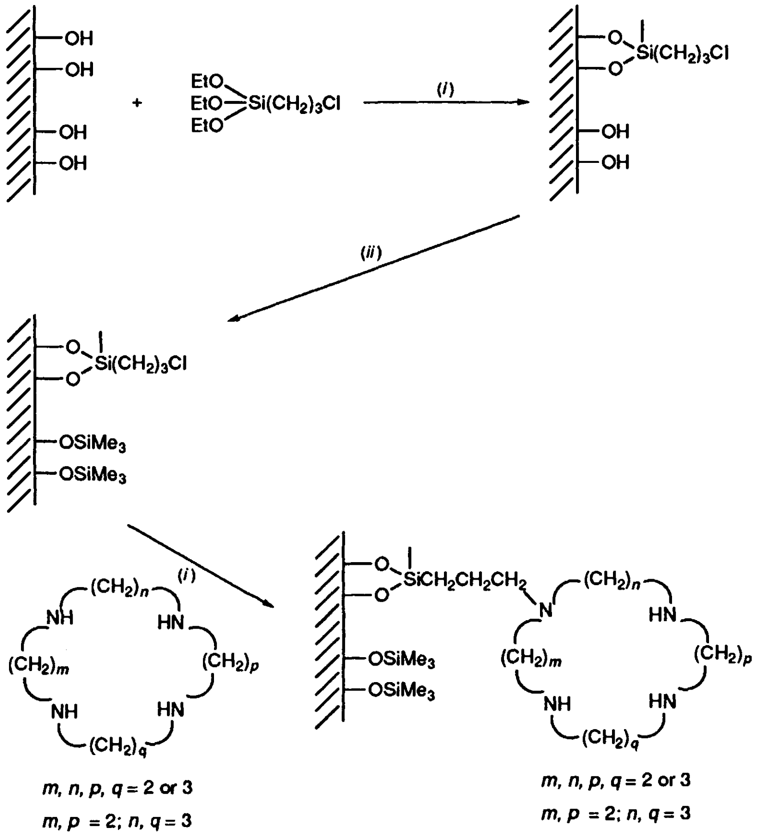
End-capping of unreacted silanol groups. The end-capping was done as in method 2.

Polyazacycloalkane attachments. A solution of polyazacycloalkane (1.0 g) in water ($100 cm^3$) was added to modified silica gel (5.0 g). The suspension was then heated at 80 °C for 48 h without stirring. Occasionally, the mixture was gently stirred or carefully shaken to prevent damage to the particles. The excess of macrocycle was filtered off and the support was thoroughly washed as in method 2 (yield 5.2 g).

Capacity determinations

Three different methods were used for capacity determinations of metallated forms of polyazacycloalkanes: quantitative ESR measurements of copper(II) complexes, nitrogen, carbon and copper elemental analysis and UV/VIS measurements.

Quantitative ESR measurements. Reaction of modified silica gel with copper(II) acetate leads to the corresponding copper(II) complex which can be studied by ESR spectroscopy. Under typical conditions the limit of detection of paramagnetic centres is close to 10^{-10}–10^{-8} mol in 1.0 g of modified polymer. These paramagnetic species are sufficiently stable to be readily observed at room temperature in the solid powder. Quantitative measurements were made using the second integral of the ESR curve. First, five copper(II) cyclam complex standards were prepared in order to determine the number of paramagnetic centres by double integration of the ESR spectrum (Fig. 1). Copper(II) cyclam was first prepared by addition of 1 equivalent of 1,4,8,11-tetraazacyclotetradecane (5.00 g, 2.50×10^{-2} mol) to 1 equivalent of copper(II) acetate monohydrate (5.03 g, 2.50×10^{-2} mol) in absolute methanol ($50 cm^3$). After 15 min, evaporation of the solvent and drying under vacuum yielded quantitatively the copper(II) complex as a purple solid, the high complex formation constant ensuring complete metallation of the macrocycle.[17–19] This complex was then diluted to different concentrations (1.00×10^{-4}–5.00×10^{-4} mol g^{-1}) in Kieselgel 60 (Merck). Samples were placed inside a double-resonance



Scheme 2 (*i*) Xylene, reflux, 24 h; (*ii*) $SiMe_3Cl$, reflux, 4 h

cavity and spectra were recorded at microwave powers which did not cause saturation of the signal. The sample was placed in the front cavity while a 3.00×10^{-4} mol g^{-1} standard was in the back cavity. Spectra of each of the standards and of the compounds (Fig. 2) were recorded by varying the packing of 0.500 g sample. It is interesting that at room temperature and in the solid state it is not possible to observe superhyperfine splitting. To correct for density differences, the double integration of the ESR signals was plotted as a function of the height of the silica in the cell. Measurements and double integrations of the front and back resonant cavities were alternatively performed to check the stability of the microwave *versus* time. Moreover, it should be noted that no free copper(II) was detected by ESR spectroscopy, implying that no metal traces can be responsible for any observed signal.

Complexation of tetraazamacrocycles bonded to silica. Typically, copper(II) complexes were prepared by addition of a saturated methanolic solution of copper(II) acetate monohydrate to a methanolic mixture of the modified silica gel. To ensure correct metallation of the ligand, the macrocycle co-ordinating atoms have to be deprotonated. This mixture was then allowed to equilibrate for 30 min, after which the silica gel was filtered off, washed several times with methanol and dried under vacuum.

Quantitative UV/VIS measurements. An indirect determination of the amount of co-ordinated and adsorbed copper(II) can also be made by UV/VIS measurement. First, modified silica (0.800 g) was treated with an aqueous solution (15 cm^3) of $Cu(O_2CMe)_2{\cdot}H_2O$ (5×10^{-2} mol dm^{-3}) for 30 min. After centrifugation, UV/VIS spectra of the solution were recorded at $\lambda_{max} = 760$ nm ($\varepsilon = 26.11$ dm^3 mol^{-1} cm^{-1}). Difference in the copper(II) concentrations in solution before and after loading ($\Delta c = c_1 - c_2$) corresponded to the uptake of copper (Table 1).

Table 1 Comparison of copper(II) uptakes (mmol g^{-1}) using the three methods of quantification

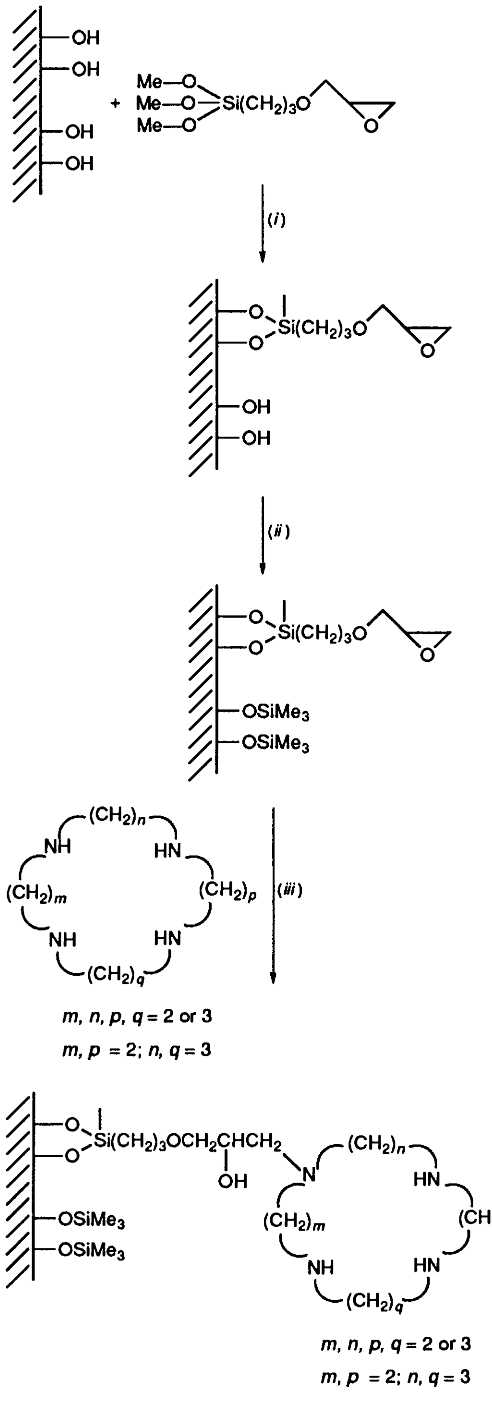
Grafted macrocycle (by method 3)	UV/VIS	ESR	Elemental copper(II) analysis
L^1 (cyclen)	0.38	0.26	0.24
L^2 (cyclam)	0.41	0.29	0.29
L^3	0.23	0.13	0.12

Results and Discussion

Synthesis

Silica gel is generally represented as a condensation polymer of silicic acid $Si(OH)_4$ implying that its surface is comprised partially of Si–OH groups. Several procedures indicate that there are between 4.6 and 8.0 silanol groups per nm^2 on silica gel, corresponding to a concentration in the range 2–5 mol kg^{-1}.[20] The silanol groups are mainly formed either in the course of the preparation, *i.e.* during the condensation polymerization of silicic acid, or as a result of rehydroxylation of dehydroxylated silica (Si–O–Si) when treated with water or aqueous solutions.[21] The pK_a of the first ionization of free silicic acid is 9.9 and it is likely that the pK_a of a surface silanol group will be fairly close to this value.[22] Consequently the silanol groups act as weak acids but form strong hydrogen bonds with water, alcohols, ethers, *etc.*, and weak ones even with olefins and benzene.

Four major factors are generally considered[23] to explain the properties of modified silica gels. These are the physicochemical characteristics of the silica gel (pore 'diameters', specific areas, pore 'volume', commercial sources and batches), phase modifications (stoichiometry, nature of the solvent, reaction time, temperature, stirring or not), the nature of the bonded ligand and the end-capping of the unreacted silanol groups.



Scheme 3 (*i*) Toluene, reflux, argon; (*ii*) $SiMe_3Cl$, reflux, 4 h, argon; (*iii*) distilled water, 48 h

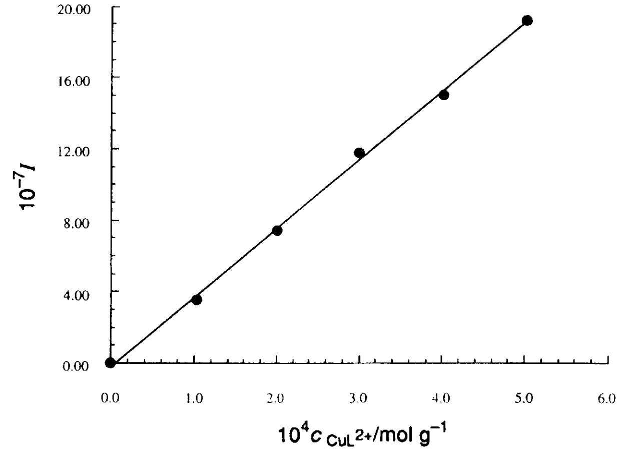


Fig. 1 Double integration of ESR spectrum as a standardizing function of concentration. Equation of straight line: $y = -0.17928 \times 10^7 + 3.8741 \times 10^{-4}x$; $R = 0.9994$

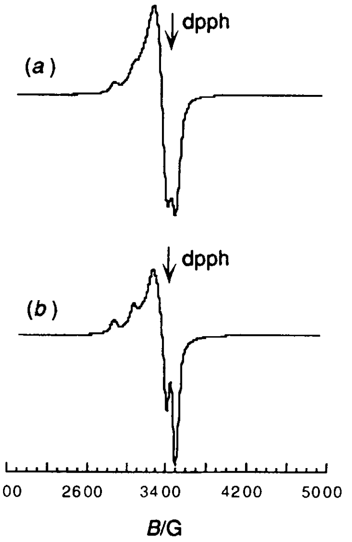


Fig. 2 The ESR spectrum of copper(II) cyclam grafted (*a*) by method 2, (*b*) by method 3. dpph = Diphenylpicrylhydrazyl; G = 10^{-4} T

Some physicochemical characteristics of the silica gels used are given in the Experimental section. As previously discussed by Berendsen *et al.*,[24] the number of the available silanol groups is sufficient to obtain average attachments of polyazacycloalkanes near to 0.5 mmol g^{-1}. Surface pre-treatment with strong acids in order to increase this number is not necessary and may not be wise, because it could introduce structural changes in the silica gel support. For the materials described in this paper no attempt was made to optimize the silylation reaction step with regard to silane concentration, solvent, reaction time, *etc.*, and it was performed in dry solvents and sealed reaction flasks. Solvents were thoroughly dried before use to avoid possible formation of siloxane polymer in the presence of traces of water. Silica gels were also heated for 12 h under high vacuum to remove major traces of water. Air trapped in the pores of the silica gels was removed using a vacuum line flushed with dry argon to facilitate reaction at the surface. Refluxing conditions were used in order to maintain air-free pores in the solid matrix.

Since the unreacted silanol groups are capable of complexing metal ions, it was desirable to end-cap these in order to determine the quantity of copper(II) co-ordinated to the macrocycle. In fact, we have observed by UV measurements that, before bonding of the macrocycle, silica gel treated by $SiMe_3Cl$ didn't take up any copper(II). In contrast, some copper(II) is adsorbed on the untreated silica gel. So, the main aim of 'end-capping' is to avoid adsorption of metal cation at the surface of the silica gel. It is generally considered[25] that only half of the silanol groups are available for reaction with chlorotrimethylsilane. The remainder are apparently located in inaccessible crevices and small pores. As the hydrophobic nature of the beads is increased by the attachment of trimethylsilyl groups, the wetting properties of the silica gel appear to be slightly modified. As previously shown by Jezorek and co-workers,[26] it is important to note that 'capping' does not destroy the groups already bound to the silica surface.

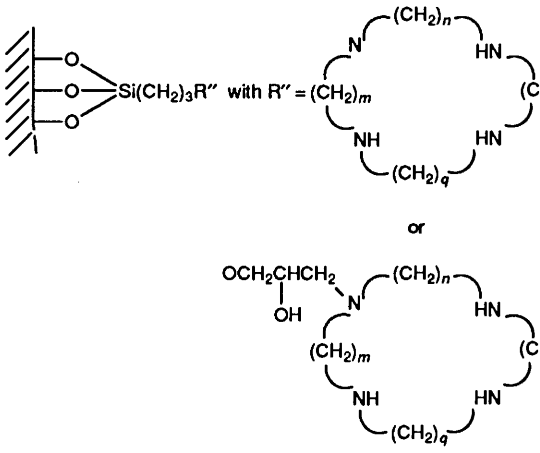
Capacity determinations

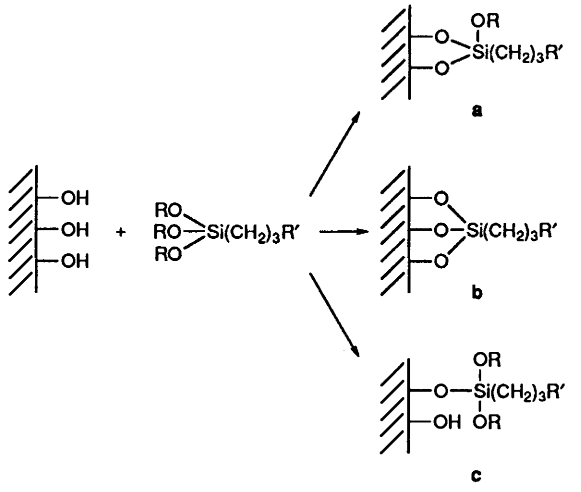
Elemental analysis were used to evaluate the number of equivalents of macrocycle bonded to the silica gel. As elemental carbon analysis is often given for commercial silica gel, the microanalysis data for the modified silica including nitrogen determination provide useful information. Nevertheless such

Table 2 Macrocycle content (mmol g^{-1}) determined by nitrogen and carbon elemental analysis

Method of attachment	Grafted macrocycle	Nitrogen	Carbon *
2	L^1 (cyclen)	0.42	0.51
	L^2 (cyclam)	0.44	0.54
	L^3	0.35	0.46
3	L^1	0.33	0.54
	L^2	0.37	0.51
	L^3	0.35	0.48

* Calculated for





Scheme 4 R = alkyl, R′ = functional group

data have to be interpreted critically. In many cases great discrepancies between calculated and experimental percentage values are observed due to too high amounts of carbon (Table 2). Similar discrepancies were reported by Jezorek *et al.*,[25] Berendsen *et al.*,[24] Unger[27] and Félix *et al.*[23] It is possible that the silanes or silicas themselves contain organic polymer possessing no nitrogen atoms.[25] A more likely explanation is that some of the initially bound silanes are not totally coupled to Si–OH groups due to steric hindrance. During the silylation stage the average composition of the products obtained was near that shown as **a** in Scheme 4.[20] However, it is also possible to have minor silylated compounds as shown in **b** and **c**. Therefore, it is not possible to know exactly the number of carbon atoms. Moreover, we did not determine the exact amount of SiMe$_3$ groups introduced during the end-capping step. For these reasons, carbon microanalysis is a poor method to determine the amount of grafted macrocycle. Another explanation of these results is possible. Indeed, the nucleophilic reaction following the silylation step is certainly incomplete. Thus, for the three methods discussed here, average attachments of polyazacycloalkanes obtained by nitrogen microanalysis (Table 3) vary from 0.33 to 0.44 mmol of macrocycle per gram of silica (in method 1, as there are already some nitrogen atoms on the silica gel surface before grafting, it is not possible to quantify the amount of bonded tetraazamacrocycle using nitrogen microanalysis). Elemental analyses indicate average amounts varying from 0.7 to 1.0 mmol of amino, chloro and epoxide groups per gram of silica, showing that some of the original functional groups do indeed remain unreacted. In each case, nitrogen microanalysis yielded lower values than those obtained by carbon microanalysis. Therefore, for all the modified silica gels prepared according to methods 2 and 3 the nitrogen percentage was used to evaluate the macrocycle content.

Copper determination and ESR measurements were subsequently used to evaluate the metal uptake (complexation amount). It is worth noting that a good agreement between elemental copper determination and ESR measurements was possible but only after 'end-capping' and thorough washing of the silica gels. At room temperature and in the solid state, the relaxation time of uncomplexed copper(II) ion is too fast to observe any signal by ESR spectroscopy. Table 3 gives a comparison of the results obtained by elemental analysis and ESR measurements. The UV/VIS copper-uptake studies were also used to determine the amount of active polyazamacrocycle. However, in most cases, this indirect back titration led to higher values than those obtained by the two other methods (Table 1). It is possible that, without thorough washings, some copper(II) is adsorbed on the silica gel surface. As has been previously reported by Lindoy and co-workers,[9] in each case the maximum copper(II) uptake is less than required to fill the calculated number of available macrocycles sites, as determined by elemental nitrogen microanalysis. However, for materials obtained following methods 2 and 3, about 73% of the macrocycle sites are occupied at 'saturation' in the case of cyclen and 77% in the case of cyclam. These values are very close to the 71% copper(II) uptake reported by Lindoy and co-workers[9] in the case of a 17-membered O$_2$N$_3$-donor macrocycle appended to a derivatized silica gel substrate. Those workers mentioned a metal-ion dependence of the uptake, very likely reflecting differential steric effects associated with the three-dimensional polymeric network. Such hindrance may reduce the ability of some sites to bind some metal ions when unfavourable induced conformational changes are observed. It may also restrict metal-ion access to particular sites. We also note that for cyclam (Scheme 3), Bagnoud *et al.*[16] reported a copper(II) uptake of 0.20 mmol per gram of silica while in our case about 0.29 mmol of copper(II) are retained per gram of silica gel.

The time necessary to accomplish complete loading of copper(II) onto the silica gel surface was approximately 30 min. Almost the same copper(II) uptake values were obtained after 72 h and the loading time appears to be, in most cases, less than 30 min.

During the coupling step, it is worth noting that the choice of functionalized groups can slightly affect the macrocycle attachment rate in methods 2 and 3. If we compare the copper(II) uptakes, it seems that the metallation constants of the bonded polyazacycloalkanes depend partly on the size of the macrocycle, since the highest values are observed for cyclen and cyclam, while the lowest one corresponds to the larger tetraazacyclohexadecane.

Conclusion

This study shows that the quantitative back titration of macrocycle grafted onto a silica gel surface can lead to higher values than those determined by direct ESR quantifications. 'End-capping' of the unreacted silanol groups has to be carried

Table 3 Comparison of the results (mmol g^{-1}) obtained for the three methods

Method of attachment	Grafted macrocycle	ESR	Elemental analysis	
		Copper content		Macrocycle content
1	L^1 (cyclen)	0.26	0.28	—
	L^2 (cyclam)	0.23	0.23	—
2	L^1	0.30	0.31	0.42
	L^2	0.30	0.27	0.44
	L^3	0.054	0.056	0.35
3	L^1	0.26	0.24	0.33
	L^2	0.29	0.29	0.37
	L^3	0.13	0.12	0.35

out in order to correlate direct and indirect determinations. Work is underway in our laboratory to optimize the silylation reaction with regard to silane concentration, reaction time, type of support, *etc.* Moreover, as shown for the tetraazamacrocycle series, the three procedures reported in this paper can be extended to the attachment of other azamacrocycles. It was shown in our laboratory that such a modified silica gel was efficient for the treatment of alpha contaminated (u, Pu, Am) liquid wastes. Moreover, it has excellent stability after several recoveries by treatment with strong acid.

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