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Synthesis and Structural Characterization of a New Macrocyclic Polysiloxane-immobilized Ligand System

Nizam M. El-Ashgar[1], **Issa M. El-Nahhal**[2,*], **Mohamed M. Chehimi**[3], **Michel Delamar**[3], **Florence Babonneau**[4], and **Jacques Livage**[4,5]

[1] Department of Chemistry, The Islamic University of Gaza, P.O. Box 108, Gaza, Palestine
[2] Department of Chemistry, Al-Azhar University, P.O. Box 1277, Gaza, Palestine
[3] ITODYS, Université Paris 7 – Denis Diderot and CNRS (UMR 7086), 75005 Paris, France
[4] Laboratoire de Chimie de la Matière Condensée, Université Paris VI and CNRS (UMR 7574), 75252 Paris, Cedex 05, France
[5] Collège de France, 75005 Paris, France

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Summary. A new porous solid macrocyclic 1,4,7,11,14-pentaazapentadecane-3,15-dione polysiloxane ligand system of the general formula P–$(CH_2)_3$–$C_{11}H_{22}O_2N_5$ (where P represents $[Si–O]_n$ siloxane network) has been prepared by the reaction of polysiloxane-immobilized iminobis(*N*-(2-aminoethyl)acetamide) with 1,3-dibromopropane. The FTIR and XPS results confirm the introduction of the macrocyclic functional ligand group into the polysiloxane network. The new macrocyclic polysiloxane ligand system exhibits high potential for the uptake of metal ions (Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}).

Keywords. Metal ions uptake; Ethylenediamine; Polysiloxanes; Immobilized P ligand systems.

Introduction

Functionalized porous adsorbents have been prepared and widely used as solid-phase extractants for removing heavy metals from aqueous media [1–5]. Intensive research has been exerted recently concerning the synthesis of new organo-functionalized polysiloxanes [6–8]. These polymeric materials can be synthesized either by immobilization of organofunctional groups onto silica surfaces [1, 3, 5] or by the sol–gel procedure involving hydrolysis and co-condensation of tetraethoxysilane ($Si(OEt)_4$) and the appropriate silane coupling agent $(RO)_3SiX$ [9] forming a three dimensional siloxane network. A variety of functionalized polysiloxane materials were prepared and their chemical structures were investigated using a number

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[*] Corresponding author. E-mail: Issaelnahhal@hotmail.com

of spectroscopic techniques including solid-state nuclear magnetic resonance (NMR) [10–13], X-ray photoelectron spectroscopy (XPS) [8, 14], and FTIR spectroscopy [8]. These polysiloxane-immobilized ligand systems find many important applications especially in catalysis, metal ion chemisorptions, and ion exchange chromatography [4, 15]. Attempts to immobilize macrocyclic ligands into silica surface were made but low ligand capacity was obtained [16]. Because of the difficulty of introducing appropriate macrocyclic ligands, a modified method was used, *i.e.* a multi-steps procedure. In the previous work we reported the synthesis of the immobilized iminodiacetic acid and immobilized iminobis(*N*-(2-aminoethyl) acetamide) polysiloxane ligand systems [6–8]. In this work we describe the preparation of a new polysiloxane macrocyclic ligand system by the reaction of polysiloxane-immobilized iminobis(*N*-(2-aminoethyl)acetamide) with 1,3-dibromopropane. The macrocyclic ligand system was well characterized using ^{13}C nuclear magnetic resonance, X-ray photoelectron spectroscopy (XPS), and FTIR spectra. The ^{13}C CP/MAS NMR was used to examine the structure of the polysiloxane-immobilized ligand groups whereas the XPS technique was used to examine the surface composition and surface interactions with ligand functional groups. The FTIR spectroscopy was used to follow the chemical changes of the multi-steps reaction. The immobilized ligand system was used for the extraction of metal ions (Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}) from aqueous solutions. The results confirm that the macrocyclic ligand showed higher potential for metal ions uptake than its precursor, iminobis(*N*-(2-aminoethyl)acetamide) polysiloxane ligand system.

Results and Discussion

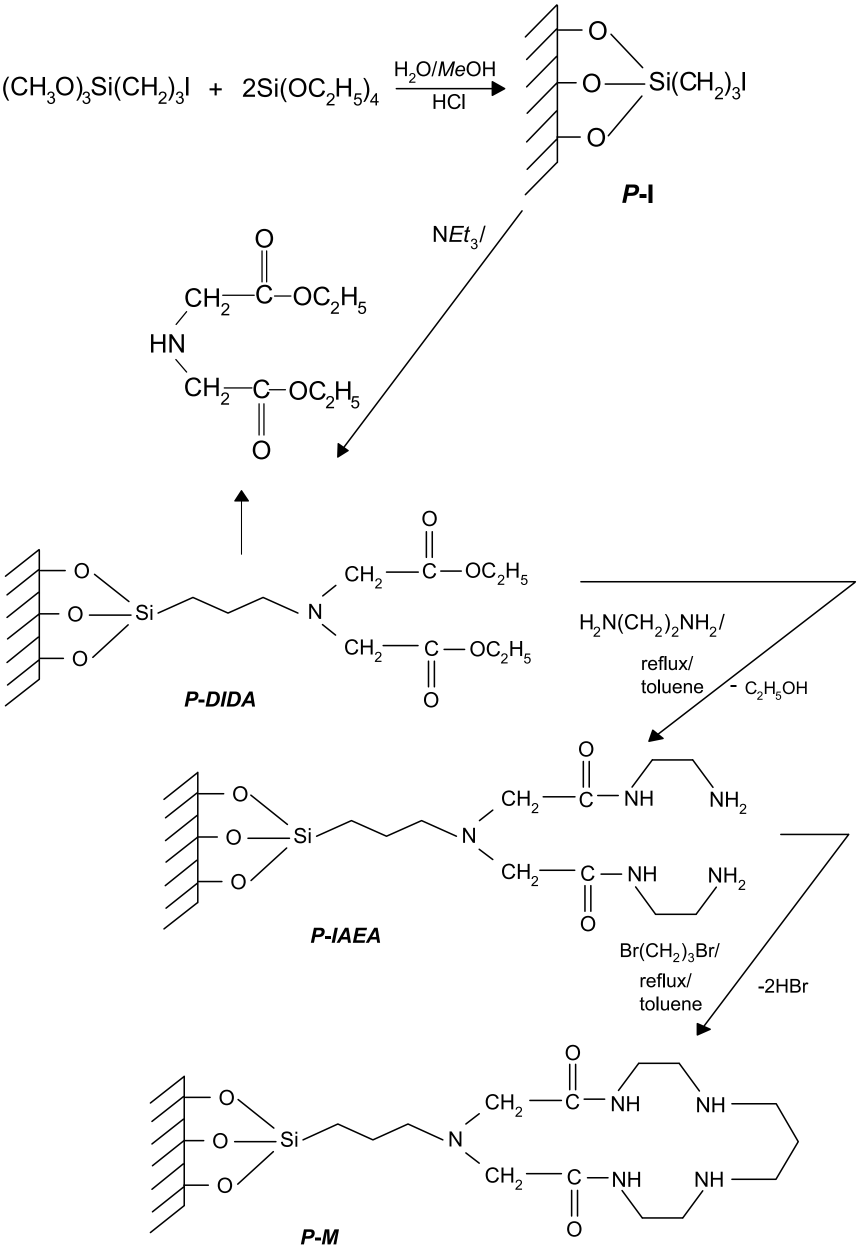
Preparation of Macrocyclic 1,4,7,11,14-Pentaazahexadecane-3,15-dione Polysiloxane Ligand System (P-M)

The functionalized polysiloxane-immobilized ligand system was prepared by multi-steps reaction based on previously prepared precursors as given in Scheme 1.

i: Preparation of 3-iododopropylpolysiloxane (*P*-I) by the sol–gel process [2].
ii: Preparation of polysiloxane-immobilized diethyliminodiacetate (*P-DIDA*) by the reaction of 3-iodopropylpolysiloxane with diethyliminodiacetate [4].
iii: Preparation of polysiloxane-immobilized iminobis(*N*-(2-aminoethyl)acetamide) ligand system (*P-IAEA*) by direct reaction of *P-DIDA* ligand system with ethylenediamine [8].
iv: The new macrocyclic ligand system 1,4,7,11,14-pentaazahexadecane-3,15-dione (*P-M*) was obtained by reaction of *P-IAEA* ligand system with 1,3-dibromopropane. The elemental analysis for the *P-IAEA* and *P-M* ligand systems are given in Table 1. The analysis shows an increase of carbon and a decrease of nitrogen percentages upon cyclization of *P-IAEA* with 1,3-dibromopropane.

FTIR Spectra

The FTIR spectra of the immobilized polysiloxane (P-IAEA) and (P-M) ligand systems show three regions of absorptions, at 3500–3000, 1750–1600, and



Scheme 1

Table 1. Elemental analysis data for the immobilized-polysiloxane *P-IAEA* and *P-M* ligand systems

Polysiloxane		%C	%H	%N
P-IAEA	Expected[#]	15.7	2.9	8.4
	Found	18.7	5.3	9.4
P-M	Expected[#]	21.4	3.6	8.9
	Found	19.9	4.7	8.5

[#] Were calculated based on the N-content in % found during analysis of the corresponding precursors

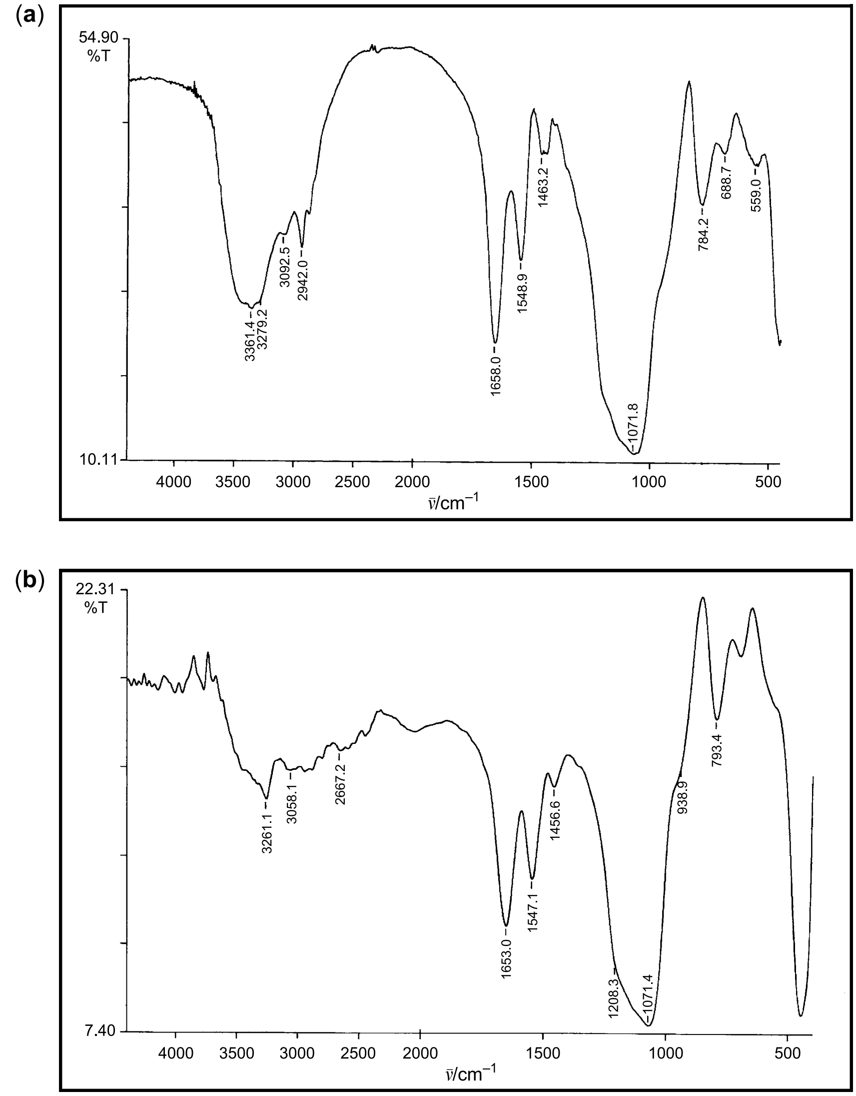


Fig. 1. FTIR spectra of a) *P-IAEA*; b) *P-M*

1200–900 cm^{-1} due to ν(OH), ν(C=O), and ν(Si–O) vibrations, respectively (Fig. 1). The FTIR spectrum for the immobilized-polysiloxane (*P-IAEA*) system (Fig. 1a) shows a strong absorption at 1658 cm^{-1} due to ν(N–C=O) of the amide group. The absence of the absorption band at 1742 cm^{-1} after treatment of the immobilized diethyliminodiacetate polysiloxane ligand system (*P-DIDA*) with ethylenediamine provides evidence for a complete reaction and that all the ethyl ester groups (–COO*Et*) were converted into the amide groups (N–C=O). This was previously confirmed [8].

The FTIR spectrum of the *P-M* ligand system (Fig. 1b) shows a significant change at 3000–3500 cm^{-1} region where a characteristic sharp band at 3261 cm^{-1} was observed and the strong broad band at 3300 cm^{-1} had almost disappeared. This can be explained due to the change of the primary amine groups (–NH_2) into secondary amine groups (–NH) and therefore ring closure is most likely.

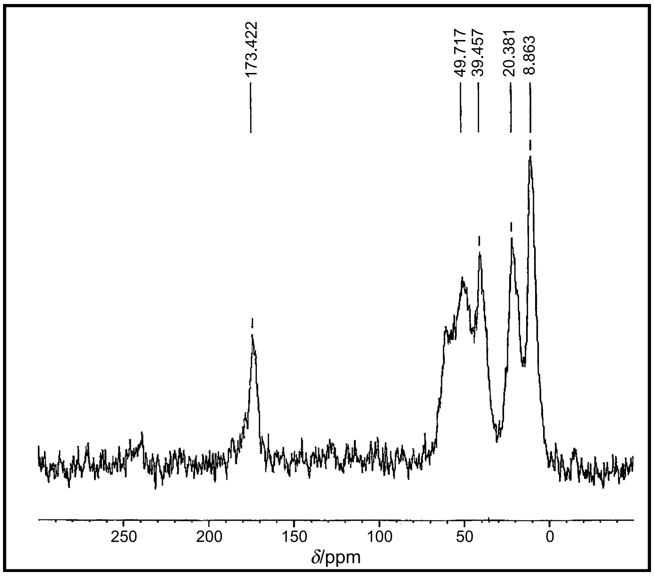
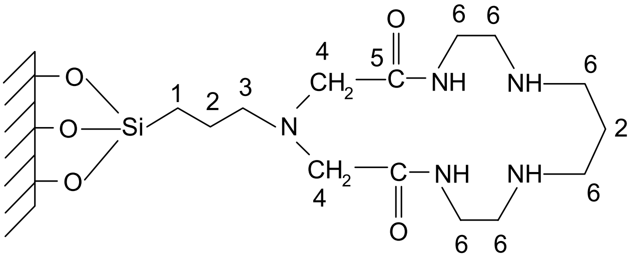


Fig. 2. ^{13}C CP-MAS NMR of *P-M*



Formula 1

NMR Studies – ^{13}C CP-MAS NMR Spectra

The ^{13}C CP-MAS NMR spectra for *P-I* and *P-DIDA* were previously reported [6–8]. The ^{13}C CP-MAS NMR spectrum for *P-M* is given in Fig. 2. The spectrum shows signals at 8.86, 20.38, and 39.45 ppm, corresponding to three methylene carbon atoms C1, C2, and C3, respectively. The spectrum also shows the methylene carbon C4 at 60 ppm and the carbonyl carbon, C5, at 173 ppm. The broad signal at 47 ppm involves six methylene carbons C6 (Formula 1). These assignments were based on literature data previously reported [6, 8, 10–13].

XPS Analysis

The XPS survey spectra for the silica-immobilized macrocyclic ligand system *P-M* and its copper(II) complex are given in Fig. 3. The XPS spectra show the main peaks at 68, 103, 285, 400, and 532 eV corresponding to Br3d, Si2p, C1s, N1s, and O1s, respectively. In Fig. 3b, the uptake of copper ions is clearly visible with the

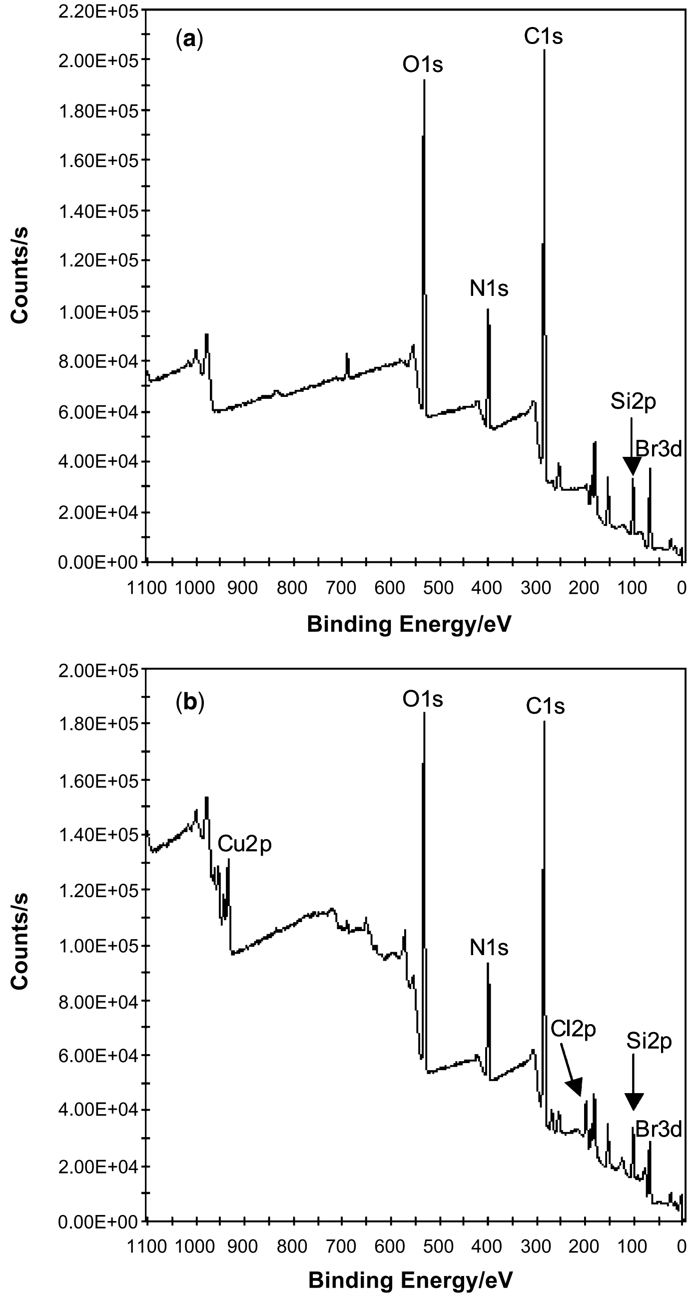


Fig. 3. XPS survey scans of a) *P-M* ligand; b) *P-M*/Cu complex

Cu2p doublet in the 933–953 eV region. The Cu2p doublet in the XPS spectra suggests that the copper is sorbed at the surface of the material and into the gel bulk. After uptake of copper ions, the survey scan in Fig. 3b exhibits also a Cl2p peak centred at 198.3 eV, assigned to chloride species (from $CuCl_2$).

It is to note that the Br3d peak is centered at 68 eV, a binding energy value that is consistent with bromides [17]. In the present case, Br3d arises most likely from HBr generated during the formation of the macro cyclic ligand.

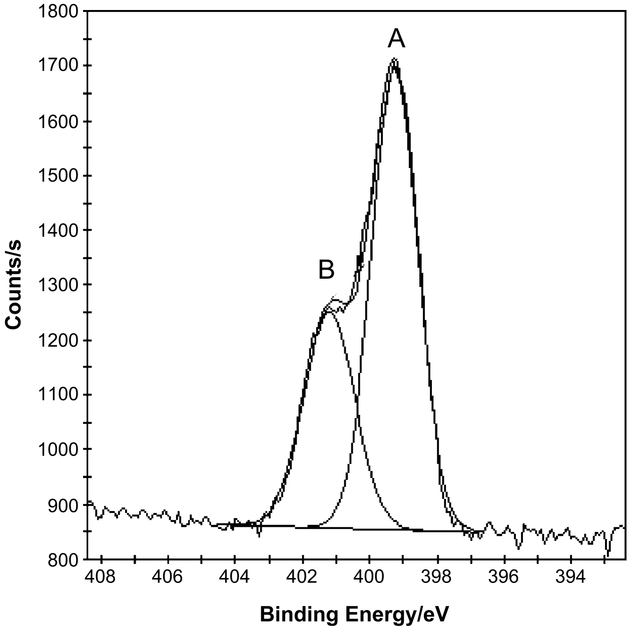


Fig. 4. High resolution N1s region of *P-M*

N1s peak shown in Fig. 4 is fitted with two components centred at 399.3 and 401.2 eV, which are assigned to free amine and strong hydrogen bonding or protonation of the amine sites. The free amines have a contribution of 68% to the total nitrogen content.

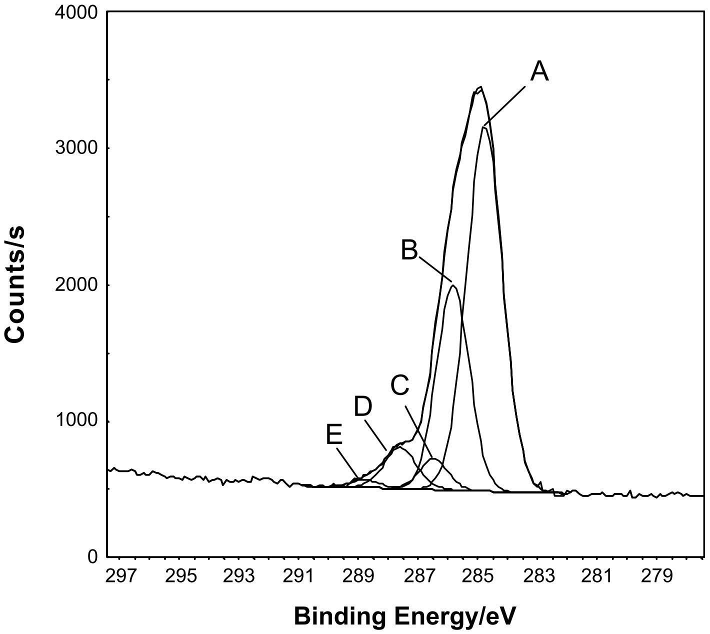


Fig. 5. High resolution of C1s region of *P-M*

Table 2. Peak fitting parameters for the high resolution C1s region of the *P-M* material

Component	BE/eV	Area/%	FWHM/eV	L/G/%
A	284.76	58.9	1.45	22.03
B	285.82	30.2	1.29	0.79
C	286.46	3.92	1.12	2.83
D	287.59	6.01	1.29	29.96
E	288.76	0.97	1.1	17.64

L/G stands for the Lorentzian to Gaussian peak shape

The C1s peak for *P-M* (Fig. 5) is broad and has several contributions from the chemical environments C–C/C–H, C–N, C–O, N–C=O, and O–C=O. The component expected at 284.1 eV from C–Si bonds is lumped with the main one due to C–C/C–H.

The peak fitting parameters of the *P-M* C1s spectrum are shown in Table 2. The minor peak centred at 288.8 eV and assigned to ester groups, may reflect the presence of some unreacted ethylacetate sites. It is interesting to note that the component B centred at 285.8 eV and due to C–N bonds has quite a high contribution to the total carbon content, thus reflecting the structure of the immobilized ligand. Interestingly, the ratio of the C1s components B (C–N bonds) and D (carbon atoms in N–C=O groups) is ~5, very comparable to the expected theoretical value of 4.5 deduced from the structure of *P-M*.

The surface composition in atomic percent is reported in Table 3. In the case of *P-M*, by considering five nitrogen atoms per macrocyclic ligand and the atomic percent of silicon and nitrogen, the ligand/Si ratio is about 0.26, that is one ligand per four silicon atoms. It is noteworthy to mention that the immobilized *P-M* system is more effective and efficient than its parent precursor (*P-IAEA*) in which the ligand/Si ratio is 0.1, that is one ligand per ten silicon atoms [8]. This result can also be deduced from the contribution of the N–C=O groups (2 per ligand) to the total carbon content and the atomic percent of silicon. The Cu/ligand atomic ratio can be deduced from the nitrogen content divided by 5 (5 nitrogen atoms per ligand) and the copper content. The value of 1.0 suggests a 1:1 copper to ligand complex.

For the *P-M*/Cu complex, the Cl/Cu atomic ratio is 1.25 whereas (Cl + Br)/Cu is 2.6, an indication that Cu^{2+} species are counterbalanced by both chlorides and bromides.

Table 3. XPS data and % surface composition of *P-IAEA*, *P-M*, and its copper(II) complex

System	Element	C	O	Si	N	Br	Cu	Cl
	Core-line	C1s	O1s	Si2p	N1s	Br3d	$Cu2p_{3/2}$	Cl2p
	BE/eV max	285	532.2	102.5	399.3	68	932.8	198.3
P-M	At.%	59.9	17.4	8.39	11.0	3.23	–	–
(*P-M*)-Cu Complex		55.8	18.6	7.47	10.6	2.79	2.12	2.64
P-IAEA [8]		42.4	28.7	19.3	9.6			

Table 4. Metal ion uptake capacity for Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} (in mmol M^{n+}/g *P-M* or *P-IAEA* ligand)

Maximum uptake of metal ion	Fe^{3+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Ref.
P-M	1.78	1.44	1.58	1.95	1.15	This work
P-IAEA	1.30	1.00	1.25	1.60	0.68	[8]

Metal Ion Extraction

The metal ion uptake capacity for Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} was determined (Table 4) by shaking the functionalized ligand system (*P-M*) with buffered metal ion solutions. An interesting observation was shown from Table 4 which is that the maximum uptake capacities of *P-M* for all metal ions are higher than those obtained with its precursor, the *P-IAEA* ligand [8]. The reason for this change is probably that cyclization reaction of functional ligands has increased the accessibility of ligand groups and therefore enhanced metal ions uptake capacity.

It is obvious from Table 3, that the copper(II) ion uptake has the highest value whereas the zinc(II) ions have the lowest value. This is probably because copper ions have a higher coordination affinity for amine ligands than zinc(II) and the other metal ions. It is clear that uptake of metal ions increases in the order: $Cu^{2+} > Fe^{3+} > Ni^{2+} > Co^{2+} > Zn^{2+}$. This is consistent with reported results of similar polsiloxane systems [8].

As the metal(II) chloride salts were used for the metal uptake extraction experiments, it is clear from the surface composition atomic percent results reported in Table 3, that the chloride counter ions are involved in coordination to the copper ion in nearly 1:1 metal to chloride.

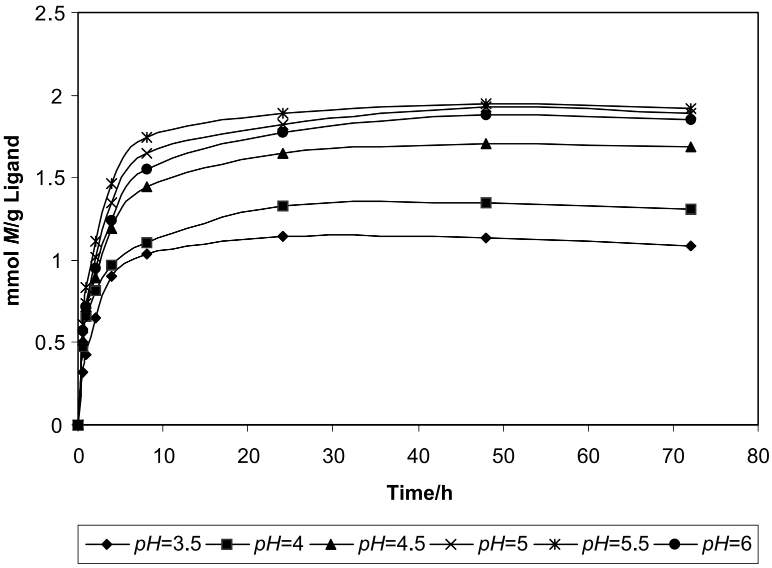


Fig. 6. Uptake of Cu(II) by *P-M versus* time

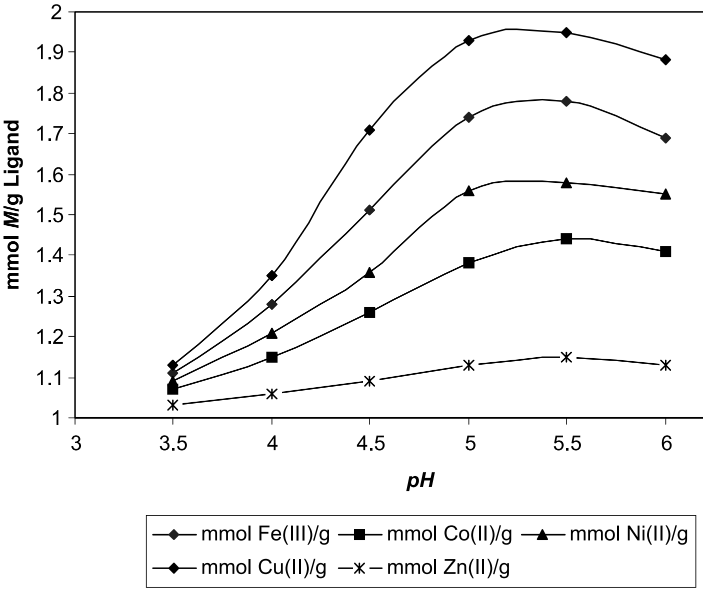


Fig. 7. Uptake of metal ions by *P-M versus pH* values (72 h shaking time)

Shaking Time Dependence

The metal ion uptake capacity (Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}) was determined by shaking the functionalized ligand system (*P-M*) with buffered solutions of the metal ions. Measurements were carried out at different time intervals. Figure 6 illustrates the uptake capacity of copper ion as an example. The results show that the metal ion uptake has reached the equilibrium after 48 hours where maximum metal ion uptake is observed. Similar results have been found for the other metal ions (Fe^{3+}, Co^{2+}, Ni^{2+}, and Zn^{2+}).

pH Dependence

The effect of *pH* on the uptake of Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} ions is shown in Fig. 7. The results show an increase of metal ion uptake with increasing *pH* reaching its maximum at $pH = 5.5$. Low metal ion uptake capacity occurs at lower *pH* values ($pH = 1$–3) due to protonation of amine species [3–7]. This reduces the ability of ligand groups to bind with metal ions. It is clear that metal ion uptake starts to decrease at higher *pH* values. This is probably due to the formation of hydrolyzed species of metal ions [18].

Conclusion

The polysiloxane-immobilized macrocyclic 1,4,7,11,14-pentaazapentadecane-3,15-dione ligand system (*P-M*) was prepared by treatment of the immobilized diethyliminodiacetate ligand system with ethylene diamine followed by 1,3-dibromopropane. The chemical structure of this system has been thoroughly characterized by means of solid state ^{13}C CP-MAS NMR, FTIR, and XPS. The results confirmed the cyclization and formation of the macrocyclic *P-M*. The immobilized ligand system *P-M* exhibits higher potential for extraction and preconcentration of metal ions (Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}) than its precursor *P-IAEA*.

Experimental

Reagents and Materials

Tetraethylorthosilicate, 3-idodopropyltrimethoxysilane, iminodiacetic acid, ethylene diamine, and 1,3-dibromopropane were purchased from Merck and used as received. Acetone, diethyl ether, and methanol (spectroscopic grade) were used as received. Salt solutions of the appropriate concentration were prepared by dissolving the metal chloride (analar grade) in deionized water. Different *pH* ranges were controlled using buffer solutions: $pH = 1–2$ was obtained using HCl/KCl buffer, $pH = 3.5–6$ by using acetic acid/sodium acetate, and $pH > 7$ by using ammonia/ammonium chloride.

General Techniques

^{13}C CP-MAS solid state NMR experiments were carried out at room temperature on a Bruker MSL-400 MHz spectrometer at a frequency of 100.6 MHz (^{13}C) using a Bruker CP-MAS probe. Proton decoupling was always applied during acquisition. Solid samples were spun at 5 kHz using 7 mm ZrO_2 rotors filled in a glove-box under dried argon. XPS signals were recorded using a VG Scientific ESCALAB 250 system equipped with a micro-focused, monochromatic AlKα X-ray source (1486.6 eV) and a magnetic lens which increases the electron acceptance angle and hence the sensitivity. The samples were mounted onto double-sided adhesives stuck onto the sample holders, and pumped overnight in the fast entry-lock at 5×10^{-8} mbar before introduction in the analysis chamber. An X-ray beam of 650 μm size was used at a power of 20 mA × 15 kV. The spectra were acquired in the constant analyzer energy mode, with pass energy of 150 and 40 eV for the survey and the narrow regions, respectively. In addition, ultimate spectral resolution was achieved for the C1s and N1s regions by setting the pass energy at 10 eV. Charge compensation was achieved with an electron flood gun combined with an argon ion gun. The argon partial pressure was 2×10^{-8} mbar in the analysis chamber. No implanted argon was detected at the surface of the materials under these conditions. With the combination of both electron and argon guns, the surface charge was negative but perfectly uniform.

The *Avantage* software, version 1.85, was used for digital acquisition and data processing. Spectral calibration was determined by setting the C1s peak maxima at 285 eV.

The surface compositions (in atomic%) were determined by considering the integrated core hole electron peak areas and their respective manufacturer's sensitivity factors.

The concentrations of metal ions in aqueous solutions were measured using a Perkin-Elmer AAnalyst-100 spectrometer.

Infrared spectra for the materials were recorded on a Perkin-Elmer FTIR spectrometer using KBr disk in the range 4000 to 400 cm^{-1}.

All *pH* measurements were obtained using a HM-40 V *pH* Meter.

All ligand samples were shaken with aqueous metal ion solutions using an ELEIA-Multi Shaker.

Preparation of 3-Iodopropyltrimethoxysilane

The 3-iodopropyltrimethoxysilane was prepared as previously described [2], where 3-chloropropyltrimethoxysilane was added dropwise with stirring to a solution of sodium iodide in dry acetone, at room temperature.

Preparation of 3-Iodopropylpolysiloxane (P-I)

Iodopropylpolysiloxane was prepared as previously reported [2] by hydrolysis and polycondensation of 3-iodopropyltrimethoxysilane with tetraethylorthosilicate in methanol, in the presence of HCl as catalyst.

Preparation of Polysiloxane-immobilized Diethyliminodiacetate Ligand System (P-DIDA)

The immobilized diethyliminodiacetate polysiloxane ligand system (*P-DIDA*) was prepared as described before [4] by treating the functionalized iodopolysiloxane with diethyliminodiacetate.

Preparation of Polysiloxane-immobilized Iminobis(N-(2-aminoethyl)acetamide) Ligand System (P-IAEA)

The polysiloxane-immobilized iminobis(*N*-(2-aminoethyl)acetamide) ligand system was prepared as described previously [8] by treating the immobilized diethyliminodiacetate with an excess of ethylenediamine.

Preparation of Macrocyclic 1,4,7,11,14-Pentaazahexadecane-3,15-dione Polysiloxane Ligand System (P-M)

Polysiloxane-immobilized system (*P-IAEA*, 5.0 g) was refluxed with an excess of 10.0 g 1,3-dibromopropane in 50 cm^3 toluene at 110°C with stirring for 48 h under nitrogen. The mixture was cooled, and the solid product was filtered off, washed with successive portions of 50 cm^3 water, methanol, and diethyl ether. The final product was dried at 90°C in vacuum (0.1 torr) for 10 h.

Metal Ion Uptake Experiments

A 100 mg sample of the functionalized polysiloxane-immobilized ligand system, (*P-M*) was shaken with 25 cm^3 0.02 *M* aqueous solution of the appropriate metal ions (Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}) using 100 cm^3 polyethylene bottles for 24 h. Determination of the metal ion concentration was carried out by allowing the insoluble complex to settle down and an appropriate volume of the supernatant was withdrawn using a micropipette, then diluted to the linear range of the calibration curve for each metal. The concentrations of metal ions in aqueous solutions were measured using a Perkin-Elmer AAnalyst-100 spectrometer. The metal ion uptake was calculated as mmol of M^{n+}/g ligand. Each study was performed at least in a triplicate. Metal ion uptake was examined *versus* shaking time (0–72 h) and *pH* (1–7).

Acknowledgements

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