Metal-Ion Extraction by Immobilised Aza Crown Ethers

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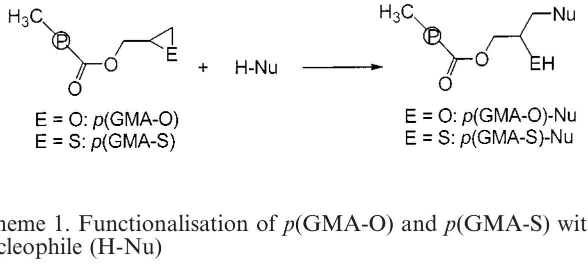
The immobilisation of [15]aneNO_4, [15]aneN_2O_3, and [18]aneN_2O_4 onto the oxirane and thiirane containing copolymers *p*(GMA-O) and *p*(GMA-S) resulted in six aza crown ether containing polymers with interesting metal-ion affinities. The pendent hydroxy or thiol groups, originating from the polymeric backbones, appeared to play an important role in the observed metal-ion affinities. The metal-ion affinity of *p*(GMA-O)-[15]aneN_2O_3 for a range of cations was found to decrease with decreasing ionic radius: $Ag^+ > Pb^{2+} > Cd^{2+} > Cu^{2+}$. The thiol-containing analogue of this polymer, *p*(GMA-S)-[15]aneN_2O_3, showed a reversed Cd^{2+}/Cu^{2+} selectivity. This illustrates the capability of pendent hydroxy groups to seriously reduce the stability of complexes of small cations compared to those of large cations. All the modified oxirane resins tested were found to be Ag^+-selective in the presence of a range of divalent (heavy) transition-metal ions. The difference in ring size between [15]aneN_2O_3 and [18]aneN_2O_4 was found to have a significant effect on the uptake values of Cu^{2+} and Zn^{2+}, as these ions are too small to fit into the ligand cavity of [18]aneN_2O_4. The uptake values for the larger Ag^+ and Pb^{2+} were found to be similar for both resins. Loaded resins were successfully regenerated (with an efficiency of 99%) by treatment with 2.0 m acid solutions (Pb^{2+} and Cd^{2+}) or with a 3.35 m NH_3 + 2.0 m NH_4NO_3 solution (Ag^+).

Introduction

Heavy-metal ions, like Cd^{2+}, Pb^{2+}, Hg^{2+}, and Cr^{3+}, exhibit toxic effects in biological systems, even at low concentration levels, as organic tissues exhibit affinity for many heavy-metal ions. Accumulation often occurs in particular organs and this results in undesired health effects.[1] Although the removal of these toxic metal ions from the environment has attracted much attention over the past decades, the pollution of surface and ground water remains a serious problem.[2] Purification systems for the removal of these toxic metal ions from aqueous solutions should possess a high degree of selectivity for heavy- and transition-metal ions due to the presence of relatively large amounts of alkali and alkaline earth metal ions in surface and ground water. Apart from toxic metal ions, those with a high commercial value also need to be recovered. Examples of these are Rh, Ir, Pd (applied in catalysis), Pt (catalysis, medicine), Ag (^{111}Ag-based immunotherapy, photographic technology), and Au (jewellery, medicine).[3]

Crown ethers are a class of ligands with metal-ion affinities that are a function of the nature, number, and spatial arrangement of the donor atoms, substitutions of the ligand backbone, the flexibility, and the hole size of the macrocycle. For instance, all-oxygen crown ethers have been found to be selective for alkali and alkaline earth metal ions, and there appears to be a correlation between ionic radius and macrocyclic cavity size.[4] The affinity of crown ethers that contain nitrogen and/or sulfur donor atoms is directed more towards (heavy) transition metal ions, and the size selectivity of this type of crown ether is much lower.[5]

Selective extraction of heavy-metal ions from aqueous solutions may be accomplished by functionalising non-hydrophobic[6] supporting materials with (multidentate) ligands, which contain donor atoms with affinity for the target metal ion(s).[7,8] In the present study, copolymers of ethylene glycol dimethacrylate (EDMA) (as the crosslinker) and glycidyl methacrylate [*p*(GMA-O)[9]], or its sulfur analogue [*p*(GMA-S)[10]] have been used as supporting materials (see Scheme 1). These polar copolymers can be functionalised easily by a ring-opening of the oxirane and thiirane moieties with nucleophiles, thereby generating additional hydroxy or thiol groups on the polymer.



Scheme 1. Functionalisation of *p*(GMA-O) and *p*(GMA-S) with a nucleophile (H-Nu)

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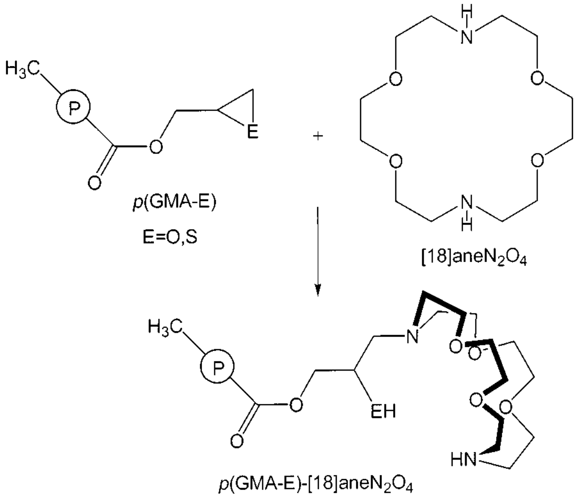
When a crown ether is used as the nucleophile, a so-called lariat ether is formed on the polymer, whereby both the crown ether and the pendent hydroxy or thiol groups may be involved in metal-ion binding. Lariat ethers are known to be very suitable for selectively binding metal ions.[11] The results of the immobilisation of the tetrathia-monoaza crown ligand [16]aneNS_4 onto both *p*(GMA-O) and *p*(GMA-S), and the metal-ion binding studies of the resulting functionalised polymers, have been reported previously.[12] Both functionalised polymers were found to have a high capacity and selectivity towards Ag^+ ions, due to the high affinity of soft sulfur atoms for soft Ag^+ ions. The affinity for Pb^{2+} and Cd^{2+}, however, was found to be much lower, as the thioether ligands on the polymers form only moderately stable complexes with these latter metal ions. To improve the extraction of these metal-ion species, the immobilisation of three macrocyclic ligands without sulfur-donor atoms, 1,4,7,10-tetraoxa-13-azacyclopentadecane ([15]aneNO_4), 1,4,10-trioxa-7,13-diazacyclopentadecane ([15]aneN_2O_3), and 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane ([18]aneN_2O_4) is reported here. In Scheme 2, the immobilisation reactions onto *p*(GMA-O) and *p*(GMA-S) are illustrated for [18]aneN_2O_4. The metal-ion uptake results, both under competitive and non-competitive conditions, the regeneration characteristics of the metal-loaded polymers, and distribution-coefficient determinations of these six functionalised polymers (**1**−**6**) are presented here.



Scheme 2. Immobilisation of [18]aneN_2O_4 onto *p*(GMA-O) and *p*(GMA-S)

Results and Discussion

Crown Ether Modified Polymers

The microanalytical data of the functionalised resins **1**−**6** are presented in Table 1. Three different batches have been synthesised for each of the resins **3** and **5**. Oxirane and thiirane conversions are relative values with respect to the oxirane and thiirane concentrations on the starting polymers. Conversions and ligand concentrations are based on the nitrogen contents of the functionalised resins. The ligand concentrations of modified thiirane resins are less accurate than those of modified oxirane resins, due to the presence of a small amount of nitrogen in the starting polymer *p*(GMA-S).

The reactivity of [15]aneNO_4 is considerably higher than that of the other two macrocyclic ligands, the ligand concentration on **1** being 1.58 mmol/g and the ligand concentrations on **3** and **5** being approximately 0.80 mmol/g and 0.60 mmol/g, respectively. The presence of unchanged oxirane and thiirane groups on the modified resins is unlikely as either methanol, that was used in the immobilisation reactions, or traces of water may have reacted with these groups. This is confirmed by the IR spectra of the resins: characteristic peaks originating from both the epoxy group {850, 910 cm^{-1} (epoxy-ring vibration) and 1340, 1480 cm^{-1} [δ(CH)epoxy]}, or the thiirane group {615, 910 cm^{-1} (thiirane-ring vibration) and 1330, 1440 cm^{-1} [δ(CH)thiirane]}, have disappeared, indicating complete conversion of the epoxy and thiirane groups.

The solid-state CP MAS ^{13}C NMR spectra of the starting polymers *p*(GMA-O) and *p*(GMA-S) and of the modified resins indicate that peaks originating from the ligands, occurring at $\delta = 70.1$ (CH_2-O), have appeared in the spectra of the modified polymers. This is in accordance with the ^{13}C NMR spectroscopic data of the free macrocycles in solution. The CH_2-N peak, found at $\delta \approx 49$ in solution, is obscured by the intense backbone peak at $\delta = 45.2$. The CH_2 (epoxy) peak at $\delta = 48.0$ and the CH_2 (thiirane) peaks

Table 1. Microanalytical data, oxirane/thiirane-group conversions, and ligand concentrations of the resins, based on the weight-% nitrogen; conversions and ligand concentrations of the modified thiirane resins are less accurate and are given in parentheses

	Resin	% C	% H	% N	% S	Conversion [%]	Ligand conc. [mmol/g]
1	*p*(GMA-O)-[15]aneNO_4	55.58	7.72	2.22		62	1.58
2	*p*(GMA-S)-[15]aneNO_4	51.84	7.01	1.32		(28)	(0.66)
3a	*p*(GMA-O)-[15]aneN_2O_3	57.30	7.47	2.29		25	0.82
3b	*p*(GMA-O)-[15]aneN_2O_3	57.05	7.46	2.48		27	0.88
3c	*p*(GMA-O)-[15]aneN_2O_3	57.38	7.47	2.03		21	0.73
4	*p*(GMA-S)-[15]aneN_2O_3	54.39	6.94	1.49	6.54	(21)	(0.44)
5a	*p*(GMA-O)-[18]aneN_2O_4	56.31	7.42	1.85		20	0.66
5b	*p*(GMA-O)-[18]aneN_2O_4	56.25	7.32	1.48		15	0.52
5c	*p*(GMA-O)-[18]aneN_2O_4	56.13	7.35	1.96		22	0.70
6	*p*(GMA-S)-[18]aneN_2O_4	51.01	6.79	1.57	7.44	(15)	(0.39)

at δ = 30.5 and 38.3 are no longer present in the spectra of the modified oxirane and thiirane resins.

Metal-Uptake Experiments

All metal-uptake experiments were performed as a function of the pH. Buffered metal chloride solutions were used for the experiments involving Cu^{2+}, Cd^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, and Ca^{2+}, whilst for the experiments involving Ag^+ and Pb^{2+} (competitive as well as non-competitive) nitrate salts were used. In these latter experiments, the pH was adjusted with dilute HNO_3 or with dilute NH_3. No Ag^+-uptake experiments were performed with modified thiirane resins, as the thiol groups on these resins are known to irreversibly bind large amounts of Ag^+ ions.[12]

Because resins **1−6** have different ligand concentrations, it would not be correct to compare the capacity values (*C* in mmol/g resin) of the different resins. Therefore, the ligand occupation (*L* in %) was calculated in order to have a more appropriate basis for comparison of the resins, where *L* (in %) = [uptake capacity (*C*) for M^{n+} (in mmol/g resin)]/[ligand concentration (in mmol/g resin)].

[15]aneNO$_4$

The metal-ion uptake results with **1** {*p*(GMA-O)-[15]aneNO$_4$} under non-competitive conditions are presented in Figure 1 (a). The maximum uptake of Ag^+ is 0.74 mmol/g at pH = 6.6 (47% ligand occupation), and is clearly a function of the pH. Cd^{2+} is the only other metal ion that is extracted significantly, although the maximum uptake is only 0.22 mmol/g at pH = 1.2. The Cd^{2+} uptake is probably due to the binding of polychlorocadmates to the resin.[12−14] The Ca^{2+} and Na^+ uptakes have also been determined, since oxa crown ethers are known to form stable complexes with alkali and alkaline earth metal ions, but no uptake was observed.

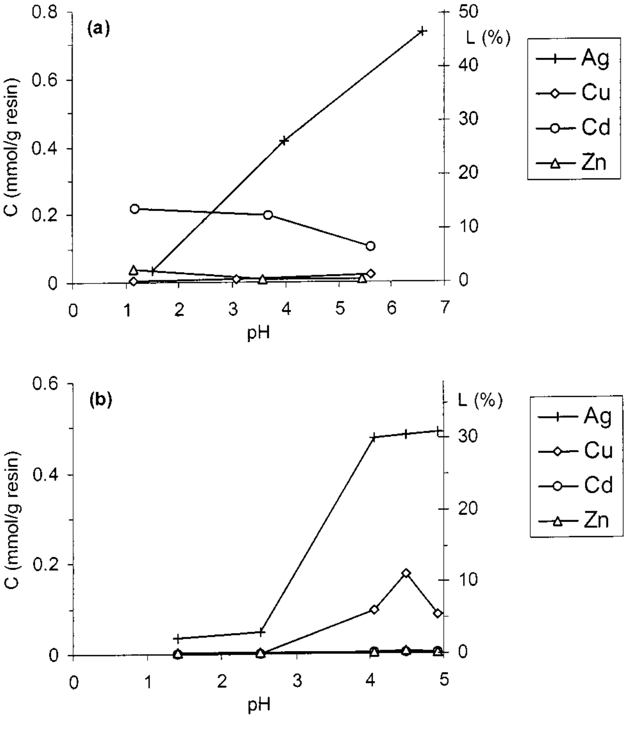


Figure 1. Metal-ion uptake behaviour of **1** {*p*(GMA-O)-[15]aneNO$_4$}: a) under non-competitive conditions; b) under competitive conditions, using metal nitrates

The experiment under competitive conditions (using metal nitrates) shows that Ag^+ is the predominantly adsorbed species, although some Cu^{2+} is also extracted, see Figure 1 (b). This Cu^{2+} uptake is not in agreement with the non-competitive experiment, where no Cu^{2+} uptake was observed. The most likely explanation for this phenomenon is that the high acetate concentration in the non-competitive experiment (originating from the buffer) prevents the binding of Cu^{2+} to the ligands on the resin, as these acetate ions themselves are relatively strong ligands for Cu^{2+}. The absence of an acetate buffer in the competitive experiment thus allows Cu^{2+} ions to bind to the resin. The competitive experiment also shows that, at low pH, no Cd^{2+} is taken up. This behaviour is in agreement with the hypothesis that the Cd^{2+} uptake in the non-competitive experiment is due to the formation of polychloro species, as chloride ions were present in the non-competitive experiment and absent in the competitive experiment.

The capacity of modified thiirane resin **2** was determined for Cu^{2+}, Cd^{2+}, Zn^{2+}, and Ca^{2+}. The maximum uptake values of these metal ions were found to be 0.19 mmol/g, 0.18 mmol/g, 0.12 mmol/g, and 0.03 mmol/g, respectively. A significant part of this uptake, however, can be ascribed to the thiol groups on the resin. This is suggested by blank experiments with a resin containing only thiol and hydroxy groups, which showed an uptake of 0.14 mmol/g Cu^{2+} and 0.09 mmol/g Cd^{2+}. The competitive experiment with **2** shows that the resin is moderately Cu^{2+} selective, the maximum uptake being 0.15 mmol/g at pH 6.0.

[15]aneN$_2$O$_3$

The uptake results with **3b** {*p*(GMA-O)-[15]aneN$_2$O$_3$} under non-competitive conditions are presented in Figure 2 (a). The highest uptake is observed for Ag^+, 0.52 mmol/g at pH = 6.4 (ligand occupation of 59%). The metal uptake of all tested species shows a pronounced pH dependence, which is probably due to protonation of the nitrogen atom(s) of [15]aneN$_2$O$_3$ at low pH. In fact, Cd^{2+} is the only species that is adsorbed at low pH. The Cd^{2+} uptake at high pH is slightly lower than the Pb^{2+} uptake, but it clearly exceeds the uptake of Cu^{2+}. The observed order in the metal-uptake values, $Ag^+ > Pb^{2+} > Cd^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+} \approx Ni^{2+}$, is different from the order found for the formation constants of complexes of the free macrocycle [15]aneN$_2$O$_3$ with these metal ions in aqueous solution: $Cu^{2+} > Cd^{2+} > Pb^{2+} \approx Ag^+ > Zn^{2+} > Co^{2+} > Ni^{2+}$.[15] In contrast, the order of stability constants of these cations with two structurally related cryptands (see Figure 3) in aqueous solution was found to be $Ag^+ > Pb^{2+} > Cu^{2+} > Cd^{2+}$, Zn^{2+}, Co^{2+}, Ni^{2+} for cryptand-211, and $Pb^{2+} > Ag^+ > Cd^{2+} > Cu^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+}$ for cryptand-221.[15] The difference between the order of the stability constants of crown ether [15]aneN$_2$O$_3$ on one hand, and resin **3b** and cryptands-211 and -221 on the other hand, must be due to the presence of additional oxygen-

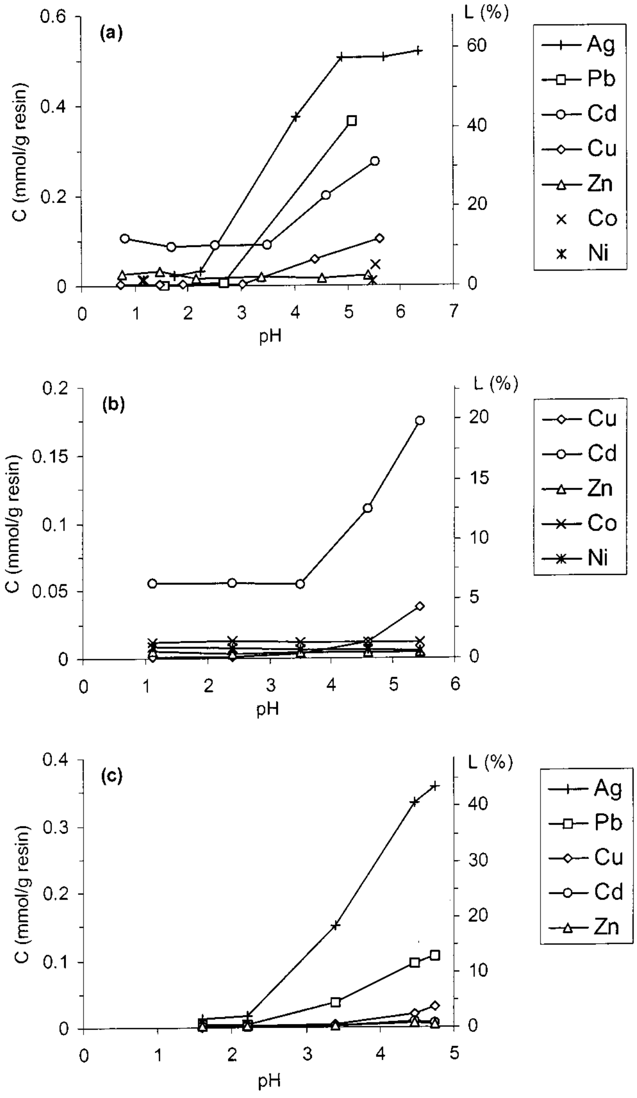


Figure 2. Metal-ion uptake behaviour of **3b** {*p*(GMA-O)-[15]aneN_2O_3}: a) under non-competitive conditions; b) under competitive conditions using metal chlorides; c) under competitive conditions using metal nitrates

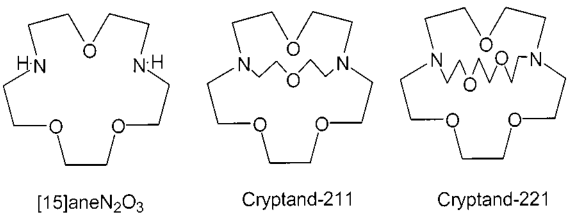


Figure 3. Structural formulae of [15]aneN_2O_3, cryptand-211 and cryptand-221

donor atoms on resin **3b** (the hydroxy groups originating from the backbone) and on the cryptands. These additional oxygen donors may change the stability of the different metal complexes.

The metal uptake by **3b** seems to be related to the ionic radii of the metal-ion species, as the metal uptake decreases with decreasing ionic radius, see Table 2. Exceptions to this trend are Ag^+ and Cu^{2+}. The relatively high value for Ag^+ can be explained by the different valencies of the tested metal ions. Ag^+ is the only monovalent species, and a higher uptake may be explained by the fact that only one negative charge has to be compensated for upon coordination, either by deprotonation of the immobilised ligand, or by the coordination of an accompanying anion. The somewhat high uptake of Cu^{2+}, compared to Co^{2+}, Zn^{2+}, and Ni^{2+}, can be ascribed to the high affinity of Cu^{2+} for nitrogen ligands.

Table 2. Ionic radii and uptake values for **3b** {*p*(GMA-O)-[15]aneN_2O_3}; ionic radii are all appropriate for coordination number 6

	Ionic radius [Å]	Uptake by **3b** [mmol/gram]
Pb^{2+}	1.19	0.36
Ag^+	1.15	0.52
Cd^{2+}	0.95	0.27
Co^{2+}	0.75	0.05
Zn^{2+}	0.74	0.02
Cu^{2+}	0.73	0.10
Ni^{2+}	0.69	0.01

The size-selective uptake by **3b** {*p*(GMA-O)-[15]aneN_2O_3} may be explained by the presence of the pendent hydroxyethyl groups, originating from the backbone. This additional coordinating oxygen donor imposes extra steric crowding on a metal ion that is already coordinated by the crown ether, and this steric crowding is best accommodated by the largest metal ions, whereas the stability of the complexes of small ions, such as Cu^{2+} and Zn^{2+}, is seriously reduced.[16,17] This results in the observed selectivity for Cd^{2+} over Cu^{2+}, Cd^{2+} over Zn^{2+}, and Pb^{2+} over Zn^{2+}. This effect is similar to the observed higher stability of large cations with the cryptands-211 and -221 in comparison with the parent macrocycle [15]aneN_2O_3.[15] The effect of the addition of hydroxyalkyl groups to oxa-aza ethers on the stability of the corresponding metal-ion complexes has been described in several papers.[16–18]

The selectivity for Cd^{2+} over Cu^{2+} is illustrated by the results of the competitive experiment, using metal chlorides [see Figure 2 (b)]. Hardly any Cu^{2+} is adsorbed between pH = 1 and 4.6, and only at pH = 5.4 some Cu^{2+} was found to be co-extracted with Cd^{2+}. The selectivity for Cd^{2+} over Cu^{2+} at pH = 4.6 is 10:1.

The selectivity for Cd^{2+} over Cu^{2+} and for Cd^{2+} over Zn^{2+} has been further investigated. In the presence of a tenfold excess of Cu^{2+}, the Cd^{2+} selectivity at pH = 4.9 is reduced to only 1.8:1, and at pH = 5.9 this is only 0.8:1, which suggests that an excess of Cu^{2+} causes a severe decrease in the Cd^{2+} selectivity. The selectivity for Cd^{2+} over Zn^{2+} is of interest as these species belong to the same group of the periodic table and hence often occur together in nature. The Cd^{2+}/Zn^{2+} selectivity in the competitive experiment, with equal amounts of Cd^{2+} and Zn^{2+} ions, is as high as 37:1 at pH = 5.4 [see Figure 2 (b)]. In an experiment at pH = 5.8, with Zn^{2+} present in a tenfold excess, the

Cd^{2+}/Zn^{2+} selectivity appears to still be 8.8:1. *p*(GMA-O)-[15]aneN$_2$O$_3$ thus exhibits a very reasonable selectivity for Cd^{2+} over Zn^{2+}, which can be ascribed to the difference in octahedral ionic radii (0.95 Å versus 0.74 Å). Similarly, cryptand-221 was reported to form complexes with Cd^{2+} and Zn^{2+} which significantly differ in stability, log*K* being 10.04 in the case of Cd^{2+} and 5.41 in the case of Zn^{2+}.[15] For [15]aneN$_2$O$_3$, the difference in log*K* values was found to be much smaller: 6.46 for Cd^{2+} versus 5.19 for Zn^{2+}.

The result of the competitive experiment, using metal nitrates, is depicted in Figure 2 (c). The same trend as under non-competitive conditions is observed: **3b** {*p*(GMA-O)-[15]aneN$_2$O$_3$} predominantly adsorbs Ag^+, although some Pb^{2+} is co-extracted at higher pH. The Ag^+ uptake at pH = 4.7 is 0.36 mmol/g.

The results of the non-competitive experiment with **4** {*p*(GMA-S)-[15]aneN$_2$O$_3$} are presented in Figure 4 (a), and show that the Cu^{2+} uptake exceeds the Cd^{2+} uptake. No correlation between the uptake and the ionic radii of the metal ions is observed, indicating that the role of the pendent thiol groups is entirely different from the role that pendent hydroxy groups play. The coordination of these thiol groups enhances the stability of the Cu^{2+} complex on the resin more than that of the Cd^{2+} complex. The maximum uptake of Cu^{2+} is 0.24 mmol/g (at pH = 5.7), for Cd^{2+} this is 0.18 mmol/g (at pH = 5.6). The experiment, under competitive conditions [Figure 4 (b)], shows that *p*(GMA-S)-[15]aneN$_2$O$_3$ is Cu^{2+}-selective in the presence of other divalent metal chlorides. Upon changing the polymeric backbone from *p*(GMA-O) to *p*(GMA-S), a reversed Cu^{2+}/Cd^{2+} selectivity is obtained, which can only be ascribed to the different effect that the pendent hydroxy and thiol groups have on the stability of the complexes formed on the resins. The donor strength of thiol groups towards (heavy) transition metal ions is higher than that of hydroxy groups, and this bond strength effect predominates any destabilising steric effect of the additional donor groups. In other words, the Cu^{2+} complex on *p*(GMA-S)-[15]aneN$_2$O$_3$ is stabilised by the pendent thiol group, where, in the case of *p*(GMA-O)-[15]aneN$_2$O$_3$, the steric effect of the pendent hydroxyethyl group predominates the bond strength effect of this group.

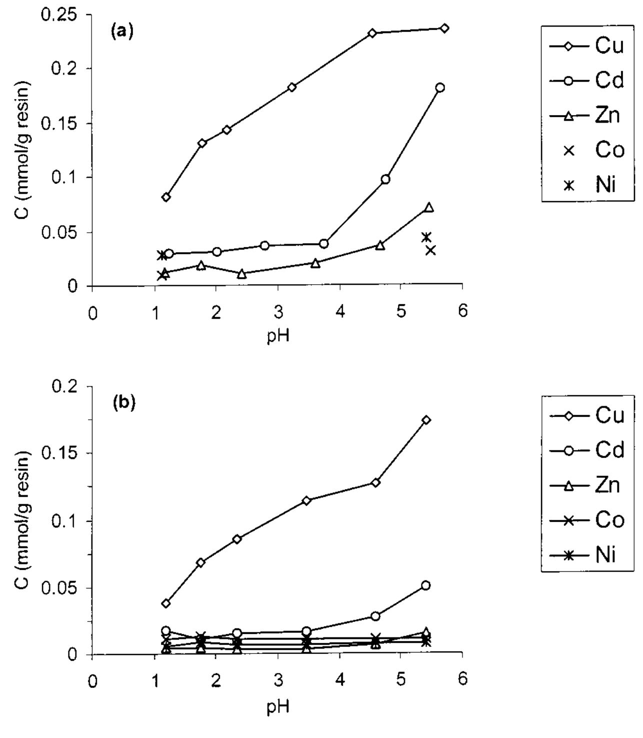


Figure 4. Metal-ion uptake behaviour of **4** {*p*(GMA-S)-[15]aneN$_2$O$_3$}: a) under non-competitive conditions; b) under competitive conditions using metal chlorides

[18]aneN$_2$O$_4$

A range of metal ions has been tested under non-competitive conditions with **5a** {*p*(GMA-O)-[18]aneN$_2$O$_4$}, see Figure 5. The metal-ion uptake values are in the order $Ag^+ > Pb^{2+} > Cd^{2+} > Cu^{2+}$, Zn^{2+}. The solution data[15] are somewhat different as in this case the Cu^{2+} complex was found to be more stable than the Cd^{2+} complex, which again may be due to the presence of the additional hydroxyethyl groups on the polymer, which destabilises the Cu^{2+} complex. The uptake of Ag^+ and Pb^{2+} is very similar to that of **3b**. The uptake curves again show a pH dependence, and the maximum uptake of Ag^+ is again higher than that of Pb^{2+}, 0.61 mmol/g for Ag^+ at pH = 6.4 (ligand occupation of 92%) vs. 0.37 mmol/g for Pb^{2+} at pH = 5.1 (ligand occupation of 56%). The ligand occupations of Ag^+ and Pb^{2+} are (slightly) higher than those found with **3b**, suggesting that the larger macrocyclic cavity slightly enhances the stability of the Ag^+ and Pb^{2+} complexes. This effect was also observed for [18]aneN$_2$O$_4$ in solution.[15] The Cd^{2+} capacity of **5a** is lower than that of **3b** and is not a function of the pH. The uptake at low pH (pH = 1 and 2), which may be due to polychlorocadmate complexes (such as $[CdCl_4]^{2-}$), is higher than for resin **3b**, suggesting that this complex anion fits better into the larger binding cavity of **5a**. At increasing pH, no increased Cd^{2+} uptake is observed, which suggests that the Cd^{2+} ion cannot effectively be accommodated in the ligand cavity of *p*(GMA-O)-[18]aneN$_2$O$_4$. Cu^{2+} and Zn^{2+} are not extracted at all by **5a**, which is an illustration of the fact that they are too small for the macrocyclic cavity of [18]aneN$_2$O$_4$.

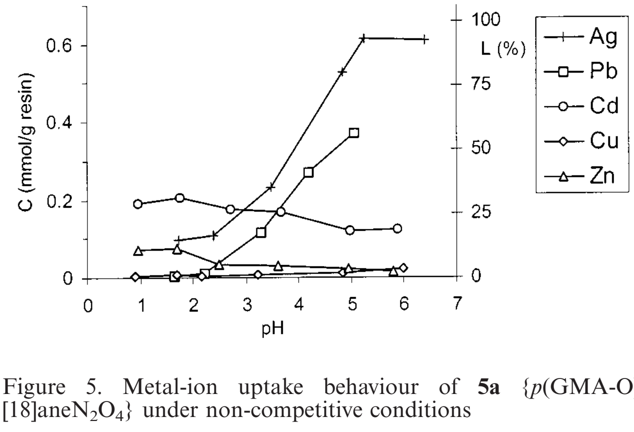


Figure 5. Metal-ion uptake behaviour of **5a** {*p*(GMA-O)-[18]aneN$_2$O$_4$} under non-competitive conditions

[18]aneO_6 is known to have a high affinity for K^+ and, to a lesser extent, for Na^+. The uptake of these two species by *p*(GMA-O)-[18]aneN_2O_4 was therefore investigated and appeared to be remarkably low, the maximum value for K^+ being 0.03 mmol/g at pH = 6.2.

The competitive experiment with **5a**, using the chlorides of Cu^{2+}, Cd^{2+}, Zn^{2+}, Co^{2+}, and Ni^{2+}, shows hardly any metal uptake at all. Only some Cd^{2+} is extracted over the whole pH range, the maximum uptake being only 0.09 mmol/g at pH = 1.7. This illustrates that these metal-ion species are too small to be accommodated in the macrocyclic cavity of [18]aneN_2O_4, and thus form very weak complexes with the resin. The competitive experiment using metal nitrates shows that both Ag^+ and Pb^{2+} are extracted, albeit to a small extent. The maximum values for these ions at pH = 4.8 are 0.17 mmol/g and 0.15 mmol/g, respectively.

The capacity of the modified thiirane resin **6** has been determined under non-competitive conditions, using buffered metal chloride solutions of Cu^{2+}, Cd^{2+}, Zn^{2+}, Co^{2+}, and Ni^{2+}. The maximum uptake values for all these metal-ion species has been observed at pH = 5.5, the values being 0.29 mmol/g, 0.23 mmol/g, 0.10 mmol/g, 0.04 mmol/g and 0.04 mmol/g, respectively. A solution of $Pb(NO_3)_2$, of which the pH was adjusted to 4.9, has been used to determine the Pb^{2+} uptake, which appeared to be 0.45 mmol/g.

The competitive experiment, using metal chlorides, reveals that **6** extracts both Cu^{2+} and Cd^{2+}, the maximum uptake of these metals being 0.21 mmol/g and 0.10 mmol/g, respectively.

Regeneration Experiments

The small quantity of **1** {*p*(GMA-O)-[15]aneNO_4} available, allowed only one regeneration experiment. The Ag^+-loaded resin was successfully regenerated with a 1.0 M HNO_3 solution, which left only 3.0% of the initial amount of Ag^+ on the resin.

Modified oxirane resin **3c** {*p*(GMA-O)-[15]aneN_2O_3} was loaded with Ag^+, Pb^{2+}, and Cd^{2+} at pH values where maximum uptake was observed in the non-competitive experiments. Aqueous solutions of acid (2.0 M HNO_3 in the case of Ag^+ and Pb^{2+}, and 2.0 M H_2SO_4 for Cd^{2+}), 3.35 M NH_3 in combination with 2.0 M NH_4NO_3, and 1.0 M $(NH_2)_2CS$ were used as potential stripping agents. The results are presented in Table 3.

Table 3. Relative amounts of residual Ag^+, Pb^{2+}, and Cd^{2+} on **3c** {*p*(GMA-O)-[15]aneN_2O_3} (in %) after stripping with 2.0 M HNO_3/H_2SO_4, 3.35 M NH_3 + 2.0 M NH_4NO_3 and 1.0 M $(NH_2)_2CS$

Stripping agent	Ag^+	Pb^{2+}	Cd^{2+}
HNO_3/H_2SO_4	5.74	0.55	1.12
NH_3 + NH_4NO_3	1.47	50.6	1.52
$(NH_2)_2CS$	16.4	37.5	14.5

The binding of metal ions by **3c** is due to the coordination of amines, oxygen ethers and hydroxyethyl moieties. Dilute acid is therefore likely to be an effective stripping agent, as the metal-binding sites can easily be protonated, and may subsequently release metal ions. This appears to be the case, as the residual amounts of Ag^+, Pb^{2+}, and Cd^{2+} on the resin after treatment with acid are only 5.7%, 0.6% and 1.1%, respectively. The stripping of Ag^+, however, appears to be more successful with NH_3 + NH_4NO_3, leaving only 1.5% of the initial amount of Ag^+ on the resin. Apparently, NH_3 is able to compete with the amines of the ligands on the resin in the case of Ag^+. This is probably due to the high stability of the formed $[Ag(NH_3)_2]^+$ complexes in solution. Cd^{2+} is also successfully stripped in this way, but when stripping with NH_3 + NH_4NO_3 is attempted for the Pb^{2+}-loaded resin, 51% of the initial amount of Pb^{2+} remains on the resin.

$(NH_2)_2CS$, which appeared to be the most successful stripping agent for the removal of metal ions from resins containing [16]aneNS_4,[12] appears to be the least effective agent for the removal of Ag^+, Pb^{2+}, or Cd^{2+} from *p*(GMA-O)-[15]aneN_2O_3. Unlike *p*(GMA-O)-[15]aneN_2O_3, however, *p*(GMA-O)-[16]aneNS_4 binds metal ions through its sulfur atoms, and $(NH_2)_2CS$ appears to be particularly useful for the disruption of these metal ion−sulfur bonds. On the other hand, *p*(GMA-O)-[15]aneN_2O_3 only contains oxygen- and nitrogen-donor atoms, and therefore other stripping agents are required, such as acid or NH_3 + NH_4NO_3.

Distribution-Coefficient Measurements

Distribution coefficients were determined for Ag^+, Pb^{2+}, Cu^{2+}, and Cd^{2+} with resins **3c** {*p*(GMA-O)-[15]aneN_2O_3} and **5c** {*p*(GMA-O)-[18]aneN_2O_4}. The results are presented in Table 4 and Figure 6. The experiments were performed at pH values where maximum uptake in the non-

Table 4. log*D* values for modified oxirane resins **3c** {*p*(GMA-O)-[15]aneN_2O_3} and **5c** {*p*(GMA-O)-[18]aneN_2O_4} with Ag^+, Pb^{2+}, Cu^{2+}, and Cd^{2+}; the pH of the experiment is indicated in parentheses

Resin	Ag^+	Pb^{2+}	Cu^{2+}	Cd^{2+}
p(GMA-O)-[15]aneN_2O_3	4.65 (6.8)	3.01 (5.1)	1.57 (5.9)	2.1 (5.9)
p(GMA-O)-[18]aneN_2O_4	3.69 (5.7)	2.66 (5.4)	0.42 (5.9)	1.60 (2.1)

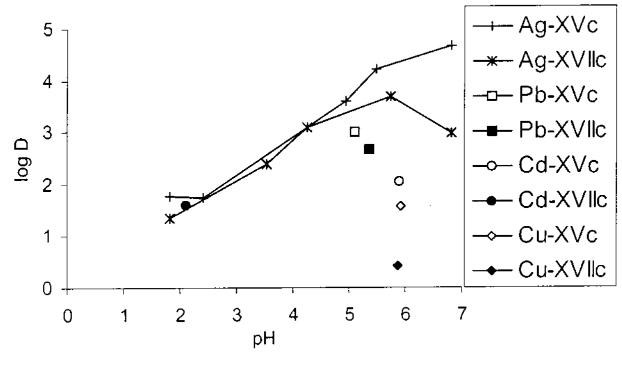


Figure 6. Distribution coefficients (log*D*) for Ag^+, Pb^{2+}, Cu^{2+}, and Cd^{2+} with **3c** {*p*(GMA-O)-[15]aneN_2O_3} and **5c** {*p*(GMA-O)-[18]aneN_2O_4}

competitive experiments was observed. In the case of Ag^+, log*D* values were determined as a function of the pH.

The results show the same trend as has been observed in the batch metal-uptake experiments: Both resins form their most stable complexes with Ag^+, and the stability is clearly a function of the pH. The stability of the Ag^+-*p*(GMA-O)-[18]aneN_2O_4 complex at pH = 6.8 is lower than at pH = 5.7, in contrast to the non-competitive uptake experiment and also in contrast to the log*D* curve of the Ag^+-*p*(GMA-O)-[15]aneN_2O_3 complex. A possible explanation for this may be that only a very small amount of Ag^+ was present in the log*D* experiments. At pH = 6.8, the small amount of NH_3 that was used to adjust the pH may have been enough to keep a significant part of the Ag^+ in solution. In the capacity measurements under non-competitive conditions, a larger excess of Ag^+ ions with respect to NH_3 was used, and the effect of the NH_3 is therefore likely to be smaller in that case.

The influence of the ring size on the log*D* values is not the same for each metal-ion species. Although the log*D* values of all metal ions are higher with *p*(GMA-O)-[15]aneN_2O_3, the difference is rather small in the case of Ag^+ and Pb^{2+}. This indicates that both the 18-membered and the 15-membered macrocycle form stable complexes with these metal-ion species. In the case of Cu^{2+}, however, the difference in the log*D* values is significant: 1.57 with *p*(GMA-O)-[15]aneN_2O_3 and only 0.42 with *p*(GMA-O)-[18]aneN_2O_4 at pH = 5.9. This illustrates once more that the cavity size of [18]aneN_2O_4 is too large for Cu^{2+}, whereas the [15]aneN_2O_3-containing resin yields somewhat more stable Cu^{2+} complexes. The log*D* value found for Cu^{2+} with *p*(GMA-O)-[16]aneNS_4 was found to be somewhat higher[12] (2.1), suggesting that the absence of thioethers in the immobilised macrocyclic ligands decreases the stability of the corresponding Cu^{2+} complexes. The log*D* values obtained for Cd^{2+} are similar to those found for *p*(GMA-O)-[16]aneNS_4.[12] These results are in accordance with chromatography experiments involving mixed-donor crown ethers, immobilised onto thin layer plates.[19] A range of macrocycles were impregnated on silica plates and mixtures of metal ions were separated on the basis of their different R_f values. The observed stability trends were $Cu^{2+} > Cd^{2+} > Ba^{2+}$ for macrocycles containing N and S donor atoms and $Ba^{2+} > Cd^{2+} > Cu^{2+}$ for those containing N and O donors.[19]

Conclusion

The immobilisation of [15]aneN_2O_3 onto *p*(GMA-O) resulted in a resin with a high capacity for Ag^+, and a somewhat lower capacity for Pb^{2+} and Cd^{2+}. A correlation between the ionic radii and the uptake values was observed for a range of metal ions. With decreasing ionic radius, a decrease in metal-ion uptake was observed. This effect was not observed for *p*(GMA-S)-[15]aneN_2O_3. The size selectivity is most probably due to the presence of pendent hydroxy groups on the modified oxirane resin. These additional neutral oxygen-donor atoms are known to destabilise complexes of small metal ions more than those of larger metal ions do. This effect only becomes apparent when crown ethers without sulfur atoms are applied, since no size selectivity due to the pendent hydroxy groups was observed for *p*(GMA-O)-[16]aneNS_4 and other thia crown ether containing modified oxirane resins.[12,20] With *p*(GMA-O)-[15]aneN_2O_3, Cd^{2+} over Cu^{2+} and Zn^{2+}, and Pb^{2+} over Cu^{2+} and Zn^{2+} selectivities have been obtained.

p(GMA-S)-[15]aneN_2O_3 shows a reversed Cd^{2+}/Cu^{2+} selectivity, which is due to the presence of pendent thiol rather than pendent hydroxy groups on the resin. Thiol groups have a higher donor strength, and their stabilising effect is larger on Cu^{2+} complexes than on Cd^{2+} complexes, and loss of the Cd^{2+} over Cu^{2+} selectivity, observed for *p*(GMA-O)-[15]aneN_2O_3, is the result.

The distribution-coefficient measurements show that Cu^{2+} forms less stable complexes with *p*(GMA-O)-[15]aneN_2O_3 than with resins containing thia crown ethers.[12] This suggests that the presence of thioethers, in the macrocyclic ligands, increases the stability of the Cu^{2+}. *p*(GMA-O)-[18]aneN_2O_4 extracts amounts of Ag^+ and Pb^{2+} that are similar to *p*(GMA-O)-[15]aneN_2O_3, but the uptake of Cd^{2+}, Cu^{2+}, and Zn^{2+} appeared to be drastically reduced. The cavity size of [18]aneN_2O_4 is apparently too large to accommodate these latter metal ions. As with *p*(GMA-O)-[15]aneN_2O_3, the ionic radius of the metal ions is an important factor in the interpretation of the uptake results obtained. The increase in the cavity size of the macrocycle has its largest effect on the smallest metal ions, as the difference in the log*D* value of the small Cu^{2+} ion with *p*(GMA-O)-[15]aneN_2O_3 and *p*(GMA-O)-[18]aneN_2O_4 illustrates. For large metal-ion species, such as Ag^+ and Pb^{2+}, comparable log*D* values have been obtained for the two resins.

Regeneration experiments, performed with Ag^+-, Pb^{2+}-, and Cd^{2+}-loaded *p*(GMA-O)-[15]aneN_2O_3, showed that stripping with 2.0 M acid is successful for Pb^{2+} and Cd^{2+}. The combination of NH_3 + NH_4NO_3 appeared to be the most successful method for Ag^+. It was not possible to remove the metal ions with $(NH_2)_2CS$ from the loaded resins, in contrast to the loaded resins that contain thia crown ethers. Apparently, the type of donor atoms that bind a metal ion determines the type of stripping agent that is best applicable.

The absence of sulfur atoms in the crown ethers that have been described in the present study has resulted in selectivity patterns that are governed by several factors. The ring size of the macrocycle, the effect of the pendent hydroxy groups and the relative positions of the metal ions and the donor atoms on the HSAB scale all become important when oxygen donor atoms, which are relatively weak donor atoms for (heavy) transition-metal ions, are used in crown ether containing metal-ion extractants. This has resulted in functionalised polymers with an enhanced affinity for large heavy-metal ions such as Cd^{2+} and Pb^{2+}, compared to resins containing thia-aza crown ethers.

Experimental Section

Starting Materials: [15]aneNO$_4$ and [15]aneN$_2$O$_3$ were purchased from Aldrich, and [18]aneN$_2$O$_4$ was obtained from Fluka. All other reagents and solvents were purchased from commercial sources and were used as received, unless stated otherwise. DMF was stored under dinitrogen over molecular sieves (4 Å). Toluene was distilled from sodium metal and stored under dinitrogen over molecular sieves (4 Å). Methanol was distilled from magnesium and stored under dinitrogen over molecular sieves (4 Å).

Physical and Chemical Measurements: The metal contents of the digested samples (vide infra) of loaded resins were measured by atomic absorption spectroscopy (AAS) with a Perkin−Elmer 3100 AAS and flame emission spectrometer, using a linear calibration method. − Elemental analyses (C,H,N,S) were carried out by the Microanalytical Department of the University College of Dublin (Republic of Ireland). − Solid-state CP MAS ^{13}C NMR spectra (cross polarisation and magic-angle spinning) were recorded with a Bruker MSL-400 spectrometer, operating at 100.6 MHz for ^{13}C. The sample spinning rate was 7000 Hz. The cross-polarisation contact time was 1.0 ms, with 3−5 s recycle delays between successive scans. − ^{1}H NMR and ^{13}C NMR spectra were recorded with a 200 MHz JEOL JNM FT NMR spectrometer. Chemical shifts are quoted with respect to TMS as an internal reference.

Synthesis of the Ion Exchangers: Oxa-aza crown ethers were immobilised onto *p*(GMA-O) and *p*(GMA-S), according to the same general procedure.[12,21] The synthetic details for resins **1**−**6** are presented in Table 5. The epoxide concentration on *p*(GMA-O) was 4.21 mmol/g in all cases. The *p*(GMA-S) batch that was used for the synthesis of *p*(GMA-S)-[15]aneNO$_4$ contained 2.76 mmol thiirane groups per g, the thiirane contents of the batches used for *p*(GMA-S)-[15]aneN$_2$O$_3$ and *p*(GMA-S)-[18]aneN$_2$O$_4$ were 2.35 mmol/g and 3.00 mmol/g, respectively. The reaction temperature was 80 °C in all cases. After each immobilisation, unchanged ligand was collected, analysed by NMR spectroscopy, and re-used in some cases.

To a solution of the ligand in toluene or in a mixture of toluene and methanol (1:1, v/v), *p*(GMA-O) or *p*(GMA-S) was added (molar ratio ligand/epoxide/thiirane groups, 1.5:1) and the mixture was heated at 75−100 °C under dinitrogen for 5 d. The resulting resins were filtered off and purified by Soxhlet extraction with toluene (6 h) and ethanol (6 h), respectively. The resins were dried in vacuo at 50 °C for 16 h. Finally, the resins were conditioned with 0.5 M H$_2$SO$_4$ (30 min) and 0.5 M NaOH (30 min), washed with water and dried in vacuo at 50 °C for 48 h. The ligand concentrations of the functionalised polymers were calculated on the basis of the weight-% of nitrogen (microanalysis), whereby allowances were made for the nitrogen content of the thiirane-containing *p*(GMA-S) backbone, as traces of (thio)urea were left after the conversion of oxirane to thiirane.[10,12]

Metal-Uptake Experiments: The metal-uptake experiments, with the exception of those involving Ag$^+$ and Pb^{2+}, were performed using standard metal chloride solutions of 0.16 M and 0.6 M buffer solutions of NaCl/HCl (pH = 0.9−2.3) and NaOAc/HOAc (pH = 2.5−6.0). All experiments were performed in polyethylene bottles mounted on a shaker at room temperature. The capacities for Cu^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, and Ca^{2+} under non-competitive conditions were determined as a function of the pH. Batches of 70−100 mg of resin were used, together with a mixture of 25 mL of metal-ion solution and 25 mL of buffer. For the determination of the Cu^{2+} capacities at pH > 5, a lower Cu^{2+} concentration (10 mL of the standard Cu^{2+} solution and 40 mL of buffer) was used to prevent precipitation of Cu^{II} hydroxides. After a shaking time of 48 h, the samples were filtered, washed with water, ethanol and diethyl ether, and dried in vacuo at 50 °C.

Batch metal-uptake experiments under competitive conditions were performed with standard metal chloride solutions of Cu^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, and Co^{2+} in a pH range of 0.9 to 6. Batches of 70−100 mg of resin were used, together with a mixture of 5 mL of each metal ion solution and 25 mL of buffer. After a shaking time of 48 h, the samples were further handled as described for the non-competitive experiments.

Table 5. Synthetic details of immobilisation reactions of N,O-mixed donor crown ethers (Tol = toluene; IPA = 2-propanol; reaction time = 5 d)

Ligand	Support epoxide/thiirane	Solvent	Product (yield)
[15]aneNO$_4$ 1.85 g, 8.44 mmol	*p*(GMA-O) 1.34 g, 5.62 mmol	Tol (20 mL)	*p*(GMA-O)-[15]NO$_4$ **1** (2.04 g)
[15]aneNO$_4$ 1.09 g, 4.97 mmol	*p*(GMA-S) 1.20 g, 3.31 mmol	Tol (15 mL)	*p*(GMA-S)-[15]NO$_4$ **2** (1.26 g)
[15]aneN$_2$O$_3$ 1.00 g, 4.58 mmol	*p*(GMA-O) 0.73 g, 3.05 mmol	Tol (20 mL)	*p*(GMA-O)-[15]N$_2$O$_3$ **3a** (0.88 g)
[15]aneN$_2$O$_3$ 3.00 g, 13.7 mmol	*p*(GMA-O) 2.18 g, 9.16 mmol	Tol (50 mL)	*p*(GMA-O)-[15]N$_2$O$_3$ **3b** (2.67 g)
[15]aneN$_2$O$_3$ 4.48 g, 20.5 mmol	*p*(GMA-O) 3.25 g, 13.7 mmol	Tol (40 mL)/ MeOH (40 mL)	*p*(GMA-O)-[15]N$_2$O$_3$ **3c** (3.80 g)
[15]aneN$_2$O$_3$ 2.25 g, 10.3 mmol	*p*(GMA-S) 2.94 g, 6.87 mmol	Tol (15 mL)/ MeOH (15 mL)	*p*(GMA-S)-[15]N$_2$O$_3$ **4** (3.17 g)
[18]aneN$_2$O$_4$ 3.00 g, 11.4 mmol	*p*(GMA-O) 1.81 g, 7.62 mmol	Tol (30 mL)/ MeOH (30 mL)	*p*(GMA-O)-[18]N$_2$O$_4$ **5a** (2.20 g)
[18]aneN$_2$O$_4$ 2.60 g, 9.91 mmol	*p*(GMA-O) 1.40 g, 5.89 mmol	Tol (30 mL)/ MeOH (30 mL)	*p*(GMA-O)-[18]N$_2$O$_4$ **5b** (1.65 g)
[18]aneN$_2$O$_4$ 2.35 g, 8.96 mmol	*p*(GMA-O), 1.42 g, 5.97 mmol	Tol (20 mL)/ IPA (20 mL)	*p*(GMA-O)-[18]N$_2$O$_4$ **5c** (1.79 g)
[18]aneN$_2$O$_4$ 1.76 g, 6.71 mmol	*p*(GMA-S) 1.49 g, 4.47 mmol	Tol (25 mL)/ IPA (25 mL)	*p*(GMA-S)-[18]N$_2$O$_4$ **6** (1.57 g)

Batch metal-uptake experiments involving Ag^+ and Pb^{2+} were performed using standard metal nitrate solutions of 0.10 M. The capacities for Ag^+ and Pb^{2+} were determined with batches of 70−100 mg of resin over a pH range of 1 to 6. The pH of the metal solutions was adjusted with dilute HNO_3 and dilute NH_3, respectively. In the case of Pb^{2+}, pH values higher than 5.3 were not attainable due to precipitation of $Pb(OH)_2$. The experiments involving Ag^+ were performed under exclusion of light.

Batch metal-uptake experiments involving Ag^+ and Pb^{2+} under competitive conditions were performed using standard metal nitrate solutions (0.10 M) of Ag^+, Pb^{2+}, Cu^{2+}, Cd^{2+}, and Zn^{2+}. Batches of 70−100 mg of resin were used, together with a mixture of 10 mL of each of the metal solutions, and the pH was adjusted in the same way as in the non-competitive experiments with Ag^+ and Pb^{2+}. The samples were shaken for 48 h and further handled as described for the metal chloride experiments.

In the regeneration experiments, a range of potential stripping agents were tested for their ability to remove metal ions from loaded resins. A sufficient amount of ion exchanger was loaded with the appropriate metal ion solution and subsequently contacted with aqueous solutions of a range of acids or competing ligands, using parts of the same batch of loaded resin.

Distribution coefficients [D = (mg M^{n+}/g of dry resin)/(mg M^{n+}/mL of solution)] were determined as a function of pH according to Roozemond et al.[22] In each case, 0.2 g of resin, 25 mL of buffer solution and 25 mL of an appropriate metal ion solution, containing such an amount of metal ions that the polymer-bound ligands were present in about eightfold excess, were shaken for 48 h. In the case of Ag^+ and Pb^{2+}, no buffer solutions were used, instead the pH was adjusted with dilute HNO_3 or NH_3.

Samples for metal analysis were prepared by heating the loaded samples overnight with concentrated H_2SO_4 (reflux) and subsequently with concentrated HNO_3 until clear solutions were obtained.

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