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Solid polysiloxane ligands containing glycine- or iminodiacetate-groups: synthesis and application to binding and separation of metal ions †

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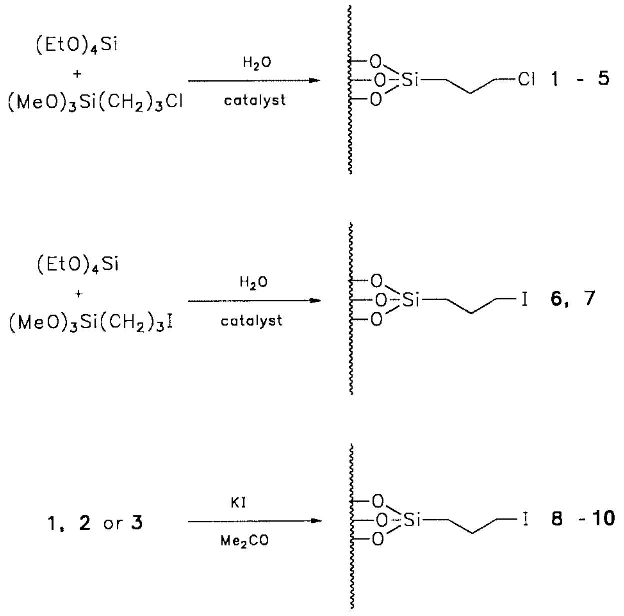
Porous solid siloxane polymers carrying glycinate or iminodiacetate ligand groups on the pore surface have been synthesised and evaluated for their binding capacities for cobalt(II), nickel(II) and copper(II). Copper(II) appears to form four-co-ordinate 2 : 1 and 1 : 1 complexes, respectively, with the two ligands. The other metals form both 1 : 1 and 2 : 1 complexes with both ligands. When used as chromatographic stationary phases, the solid ligands allow clean separation of the three metals by pH-controlled elution. Cobalt(II) and nickel(II) can also be cleanly separated by displacement–elution with copper(II).

Introduction

We have previously described various methods for the preparation of solid, porous, functionalised polysiloxane ligands.[1–4] Such materials have advantages over the more conventional organic resins in that they have good thermal and hydrolytic stability and do not swell in organic solvents. A variety of ligand groups has been employed, ranging from simple amines or phosphines to chelating di- and tri-amines and their Schiff-base and macrocyclic derivatives. Similar materials have recently been applied by others to the extraction of carbon dioxide.[5] We now describe the incorporation of chelating groups based on glycine and iminodiacetic acid and a preliminary investigation of their metal uptake and use in chromatography; clean separation of the economically important metals nickel and cobalt can be achieved. After the completion of our work, a related paper appeared,[6] the results of which are discussed in conjunction with our own.

Experimental

The 3-halogenopropyl-functionalised polymers **1**–**7** were prepared as described previously from $Si(OEt)_4$ and $(MeO)_3Si(CH_2)_3X$ (X = Cl or I) catalysed by HCl[4] or by $Bu_2Sn(OAc)_2$ (Scheme 1).[1] For **8**–**10**, halogen exchange was effected by refluxing a chloro-polymer with potassium iodide in acetone. Further details and analytical data for a selection of typical polymers is given in Table 1.



Scheme 1

Functionalisation with the ligand groups was effected by heating one of the polymers (containing 25 mmol total halogen) with sodium glycinate or disodium iminodiacetate (50 mmol) in dry (Linde 4A) DMSO (250 cm^3) at 80–120 °C for 80 hours under nitrogen. After cooling, the solid was filtered off, washed successively with DMSO, water, sodium hydroxide (0.01 mol dm^{-3}), water, hydrochloric acid (2 mol dm^{-3}), water, ethanol and diethyl ether. The solid was then dried under vacuum at 50–80 °C and kept in a vacuum desiccator. These materials are given codes **G** or **I** according to the functionality introduced.

Polymer **I3** was made by stirring solid iodo-polymer **7** (50 mmol I) with neat diethyliminodiacetate (1.0 mmol) and heating under nitrogen to 90 °C for 80 hours. The product was separated and washed with methanol and ether. The ligand in the free acid form was obtained by refluxing this solid (20 g) with hydrochloric acid (0.5 mol dm^{-3}, 250 cm^3) for 12 hours.

Analytical data for typical solid ligands are shown in Table 2. Other data are analogous.

Metal complexes were prepared by shaking (24 hours) a ligand (0.5 g) with an unbuffered aqueous solution of a metal ion (0.1 mol dm^{-3}, usually as chloride) in an amount equal to twice the total ligand content of the solid (estimated from the nitrogen content). The solid complex was separated and washed with water, methanol and diethyl ether, and dried under vacuum at 50 °C. Typical analytical data for the complexes are shown in Table 3.

Saturation capacities of the ligands were determined similarly, but by analysis of the aqueous phase before and after shaking with the ligand. Results are shown in Table 4. These last experiments were repeated with solutions buffered at various pH levels: 1 < pH < 3, hydrochloric acid–sodium acetate; 3.5 < pH < 6.5, sodium acetate–acetic acid. Ionic strength

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† *Supplementary data available*: metal-ion binding and separation data. For direct electronic access see http://www.rsc.org/suppdata/dt/1999/3463/, otherwise available from BLDSC (No. SUP 57607, 5 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).

Table 1 Analytical data for representative 3-halogenopropyl-functionalised polysiloxanes

	Ratio[a]	Catalyst	%C	%H	%Cl	%I	C/(Cl + I)[b]
1	1:1	HCl	15.9	3.6	15.3		3.1
2	1:1	HCl	15.8	4.0	15.3		3.1
3	2:1	$Bu_2Sn(OAc)_2$	13.5	3.3	11.1		3.6
4	2:1	$Bu_2Sn(OAc)_2$	14.3	3.4	11.0		3.8
5	2:1	HCl	12.5	3.2	11.9		3.1
6	2:1	HCl	10.5	2.6	0.7	32.2	3.2
7	2:1	HCl	9.7	2.4	0.8	32.7	2.9
8	**2** + KI (90 h)[c]		14.4	3.1	7.1	20.6	3.3
9	**1** + KI (7 d)[c]		13.6	2.7	4.5	31.2	3.0
10	**3** + KI (7 d)[c]		10.6	2.7	5.2	19.1	3.0

[a] Mol ratio of $(EtO)_4Si$ to $(MeO)_3Si(CH_2)_3X$ or other starting materials; for **1**–**5** X = Cl, for **6**, **7** X = I. [b] Molar ratio. [c] Excess KI in acetone.

Table 2 Analytical data for typical solid ligands

Code[a]	Precursor	%C	%H	%N	%Cl	%I	C-ratio[b]
G1	**1**	21.8	4.5	3.4	1.0	0.1	1.4
G2	**10**	15.9	4.1	2.6	0.6	0.1	1.3
G3	**3**[c]	18.1	3.6	2.1	0.4		1.9
G4	**3**[d]	13.8	3.6	1.4	3.7		1.4
G5	**6**	18.3	4.4	3.0	1.6	0.3	2.1
G6	**4**	14.3	4.1	1.6	1.4		1.7
G7	**5**	14.0	4.2	2.0	1.9		1.3
I1	**8**	19.9	4.3	1.3	2.7	0.0	1.9
I2	**10**	16.4	3.9	0.9	2.4	0.0	2.1
I3[e]	**7**	19.3	4.0	2.8			
I4	[f]	20.1	3.6	3.1			

[a] **G** = glycinate functionality, **I** = iminodiacetate functionality. [b] C-ratio = molar ratio of total carbon to carbon bound to nitrogen (C_N) and to halogen (C_X): $C_{tot}/(C_N + C_X) = C_{tot}/(5N + 3X)$ for glycinate or $C_{tot}/(7N + 3X)$ for iminodiacetate. [c] Reaction temperature 80 °C. [d] Reaction temperature 120 °C. [e] Prepared from siloxane **7** and neat diethyliminodiacetate and subsequently hydrolysed (HCl). [f] Prepared from $(MeO)_3Si(CH_2)I$ + $NH(CH_2CO_2Na)_2$ (DMSO, 90 °C, 40 h); then $(EtO)_4Si$, H_2O, $Bu_2Sn(OAc)_2$.

Table 3 Analytical data for typical metal complexes of the solid ligands

Ligand	M	%C	%H	%N	%M	N/M
G2	Cu	13.8	3.8	2.0	4.2	2.2
	Ni	15.3	4.0	2.2	3.5	2.6
	Co	15.4	4.2	2.3	2.3	4.2
I4	Cu	18.0	3.6	2.6	10.0	1.2
	Ni	19.4	3.6	2.8	8.9	1.3
	Co	19.1	3.6	2.8	7.8	1.5

Table 4 Saturation capacities of ligands in unbuffered solutions[a]

Ligand	N/mmol	Cu/mmol[b]	Ni/mmol[b]	Co/mmol[b]
G3	1.5	0.74(2.0)	0.62(2.4)	0.46(3.3)
I1	0.93	0.69(1.3)	0.56(1.7)	0.43(2.2)

[a] Estimated by determination of the metal content of unbuffered solutions before and after absorption. [b] Figures in parentheses are the molar ratios N:M.

was kept constant at 0.1 mol dm^{-3} by addition of sodium perchlorate.

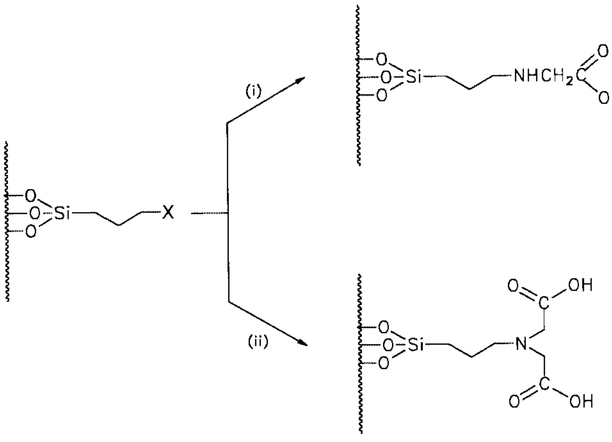
The efficiency of metal absorption was determined by shaking a large excess (20- or 40-fold) of the ligand with metal ion solutions (1.3 mmol dm^{-3}) buffered to various pH levels. [The last two sets of data are shown in more detail in the supplementary Figures (SUP 57607).]

Results

(i) The siloxane ligands

Siloxane polymers with 3-chloropropyl functionality were produced as described previously[1,4] by the hydrolytic co-condensation of the tetra- and tri-alkoxysilanes $Si(OEt)_4$ and $(MeO)_3Si(CH_2)_3Cl$ (see Scheme 1). As is usual, the polymers contain fewer functional groups than expected from the composition of the reaction mixture, indicating the formation of soluble oligomers which are lost during the washing process.[7] However, the data of Table 1 show that the preparations are reproducible (*cf.* **1** and **2**) and, as we demonstrated previously by NMR and Mössbauer spectroscopy,[2] that use of the $Bu_2Sn(OAc)_2$ catalyst leads to incorporation of the organotin group (**3**, **4**).

The pendant organochlorine groups in the polymers were converted into ligands by reaction with the sodium salts of glycine or iminodiacetic acid (Scheme 2). When carried out in hot DMSO, these reactions gave substantial replacement of the halide by the new functional group (see Table 2). As had been



Scheme 2 (i) $H_2NCH_2CO_2Na$–DMSO, HCl(aq); (ii) $HN(CH_2CO_2Na)_2$–DMSO, HCl(aq) or $HN(CH_2CO_2Et)_2$ (neat), HCl(aq).

found earlier,[4] reaction proceeds further for X = I than for X = Cl (*cf.* **G1**,**2**); similarly, more extensive reaction is obtained for the polymer based on 1 : 1 mixtures of $Si(OEt)_4$ and $(MeO)_3SiR$ than for 2 : 1 mixtures (**G1**,**7**), indicating a more open, less cross-linked structure for the former.[1] Steric inhibition is evident, in that the extent of reaction of iminodiacetate is only about half of that of glycinate. Similar observations have been made with Ph_2NH and $PhNH_2$ as nucleophile.[2]

However, problems were encountered in assessing the extent of reaction purely from microanalysis, since more chlorine appeared to be lost than ligand group introduced. This is shown in Table 2 by the molar ratio of total carbon to the sum of that bound to nitrogen (5 or 7 atoms) and to halogen (3 atoms). If the halogen groups reacted only with the nucleophile, a ratio of 1.0 would be expected: observed values are in the range 1.3–2.1. Similar results were obtained when the starting polymer was refluxed in DMSO alone, suggesting either hydrolysis by residual traces of water in the DMSO or dehydrochlorination to give 2-propenyl groups. El Nahhal *et al.*[6] have reported similar observations, although they have not evaluated the carbon ratios. They also obtained ^{13}C CPMAS NMR data which were interpreted as replacement of choride by carboxylate, including acetate. When we repeated our experiments using diethyl iminodiacetate in DMSO, we again observed a high carbon ratio [from polymer **7**, C/(11N + 3X) = 1.23]; evidently the loss of chlorine is not due to reaction with free carboxylate groups. However, when the ester was used without solvent, the loss of chlorine and gain in nitrogen were exactly in balance [for polymer **7**, C/(11N + 3X) = 1.0]. This result suggests that the previous problems came from the solvent, and is most likely to be hydrolysis due to traces of moisture: dehydrochlorination would be expected to be just as extensive with the ester as solvent as it was in neat DMSO.

The 3-hydroxypropyl groups resulting from hydrolysis would not react with the nucleophile, and this is a possible limitation to the extent of incorporation. With the ester, incorporation is 2–3 times greater without the solvent.

Best incorporation of ligand groups was obtained starting from siloxane polymers prepared from $(MeO)_3Si(CH_2)_3I$, and reached more than 70% for sodium glycinate and about 40% for sodium iminodiacetate (both in DMSO). Greater than 80% reaction was obtained using neat diethyliminodiacetate, and the resulting solid ester could be hydrolysed efficiently with hydrochloric acid (0.5 mol dm^{-3}, see ligand **I3**). This is undoubtedly the best way to introduce this grouping.

(ii) Metal uptake

(a) Batch process. Preliminary experiments established that metal uptake was usually complete within 24 hours. For glycinate-based ligands (**G1**, **G4**, **G6**), uptake of copper(II) was most rapid for polymers with the lowest ligand content and uptake was more rapid for iminodiacetate ligands (**I3**) than for glycinate. The rate of uptake increased with increase in the ligand : copper(II) mole ratio (**G4**), and was more extensive when the particle size of the polymer was reduced (for sieved **G2**, copper(II) at pH 5.0, 76% of ligand sites were occupied for 40–60 mesh and 92% for 80–100 mesh). All these observations are consistent with the presence of ligand groups with various accessibilities. Those near the surface and in large pores would react most rapidly, access to others would be diffusion controlled. Polymers containing smaller concentrations of ligand groups are more likely to have them in the most accessible sites, since they will be produced by reaction of the most readily available halogenopropyl groups. Functionalisation with iminodiacetate was shown above to be sterically controlled.

On shaking the glycinate ligands **G2**, **G3** with unbuffered solutions of copper(II), nickel(II) or cobalt(II), saturation occurred at approximately 2, 3 and 4 moles of ligand per mole of metal ion, respectively (see Tables 3 and 4). For the iminodiacetate ligands **I1**, **I4**, the corresponding figures were about 1, 1.5 and 2 moles per mole. Similar values were indicated when the pH was optimised for each metal [supplementary Fig. 1 (SUP 57607)]. At saturation, and assuming that ligand groups were appropriately placed, the normal co-ordination behaviour of these metals suggests that copper(II) would form 2 : 1 complexes with glycinate and 1 : 1 complexes with iminodiacetate (assuming normal tetragonal co-ordination), while the other metals might form six-co-ordinate 3 : 1 (glycinate) and 2 : 1 (iminodiacetate) complexes also. The preliminary results support these hypotheses but cannot, of course, distinguish the binding of two ligands to one metal ion from the situation where 1 : 1 complexes are formed and a second set of ligands is not co-ordinated. Spectroscopic data for analogous diaminoethane-functionalised systems suggests that mixtures of complexes are formed (see also below).[3]

The efficiency of extraction as a function of pH was also investigated [supplementary Fig. 2 (SUP 57607)], and shows the same trend. In both cases, the expected strengths of binding were found: $Cu^{2+} > Ni^{2+} > Co^{2+}$ and iminodiacetate > glycinate. The pH profiles were sufficiently different to give hope of effective separation of these three metals: the pH_{50} values (*i.e.* pH for 50% extraction) are 3.50, 5.85 and 7.09 for the glycinate ligand [for copper(II), nickel(II) and cobalt(II) respectively], and 1.45, 2.68 and 3.30 for the iminodiacetate ligand.

(b) Chromatographic column process. Short columns were prepared of the two types of ligand, with particle sizes in the range 60–100 mesh, and the breakthrough capacity for copper(II) was measured. For the glycinate ligand **G6** at a pH of 5.33, the breakthrough capacity increased with decreasing flowrate: 0.13 mmol g^{-1} at 56.5 cm^3 h^{-1} to 0.51 mmol g^{-1} at 5.64 cm^3 h^{-1} [further data are in supplementary Table 1 (SUP 57607)]. The latter figure is 90% of the batch-saturation capacity for this sample of ligand. The pH-dependence of the breakthrough capacity was also assessed (supplementary Table 2). The results parallel the batch experiments.

When a solution containing a mixture of metal ions was fed into the column, distinct coloured bands were formed, copper (blue) at the upstream end, nickel (green) in the centre, and cobalt (pink-red) downstream. Two methods of elution were examined: by pH control and by displacement with copper(II).

Elution of the loaded glycinate-ligand column with various buffer solutions removed cobalt(II) at pH 5.5 (Fig. 1a). Towards the end of the elution of cobalt(II) some nickel(II) began to appear in the eluate, but pH 4.5 was required to remove this ion fully. Copper(II) is removed at pH 1.0. Separation is quite clean, there being very little overlap between the three metal ions. For both cobalt(II) and nickel(II) there is a hint of two-step elution. For the iminodiacetate ligand (Fig. 1b) excellent separations are again achieved, and the two-stage elution behaviour is now very obvious.

Very similar behaviour is seen when a copper(II) solution is used as eluant to displace cobalt(II) and nickel(II) [supplementary Fig. 3 (SUP 57607)], which elute cleanly in that order. The elution curves are again asymmetric.

The asymmetry in elution peaks is best explained on the assumption of the presence of two types of complex, one more stable than the other. For iminodiacetate as ligand, these must be 1 : 1 and 2 : 1 complexes, which would be expected to be formed only for cobalt(II) and nickel(II). Copper(II), preferring to have only four tightly held ligand groups, is unlikely to form very stable 2 : 1 complexes with a dinegative tridentate such as iminodiacetate. These results agree with the levels of uptake found in the batch experiments: copper(II) is taken up in a ratio only slightly greater than 1 : 1 (ligand : metal), indicating the predominant formation of 1 : 1 complexes with a few ligand sites unoccupied, whereas both cobalt(II) and nickel(II) give

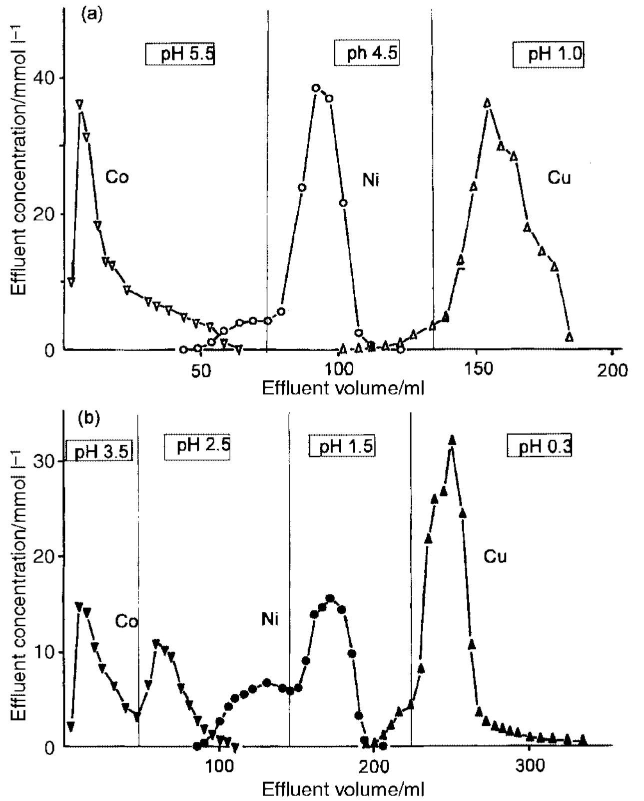


Fig. 1 Elution of cobalt(II), nickel(II) and copper(II) as a function of pH from (a) glycinate- and (b) iminodiacetate-functionalised solid ligands (**G7** and **I3**).

much higher ratios which suggest considerable formation of 2 : 1 complexes.

That analogous behaviour is less pronounced for the glycinate ligands is also understandable. In this case, the formation of 2 : 1 complexes would be expected in so far as it is allowed by the arrangement of ligand groups within the polymer. The juxtaposition of the three ligand groups needed to give six-co-ordination is much less likely.

Conclusion

The new ligands described, based on polysiloxane solids functionalised with glycinate or iminodiacetate ligand groups have good potential for the extraction and separation of metal ions from aqueous solution. In particular, clean separation of cobalt(II) from nickel(II) can be effected; this could be of value in the treatment of ores and residues where the two metals occur together and are difficult to separate by traditional methods. As with other ligands of this type, described previously,[1–4] they have good hydrolytic stability over a wide range of pH.

During the functionalisation of the starting 3-halogenopropyl group, we observed greater loss of halogen than incorporation of nucleophile. We believe this to be due to hydrolysis by traces of water in the solvent; when no solvent is employed, stoichiometric replacement is achieved. It seems unlikely that attack on an alkyl chloride should be more rapid by the relatively weakly nucleophilic carboxylate group than by an amino- or imino-group, as implied by El-Nahhal *et al.*[6] This is supported by the fact that all our samples show similar metal-uptake behaviour; this would not be the case if some involved ester-type binding of the amino-acid residues, $-(CH_2)_3-O_2CCH_2NHR'$, and other N-bound groups with free carboxylate residues, $(CH_2)_3N(R')CH_2CO_2^-$. It is the latter grouping which gives the effective binding.

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