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Insoluble ligands and their applications

IV *. Polysiloxane-bis(2-aminoethyl)amine ligands and some derivatives

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Abstract

Methods have been developed for the preparation of insoluble polysiloxane ligands containing pendant $-N(CH_2CH_2NH_2)_2$ groups and their salicylaldimine Schiff-base and cyclised derivatives. The ability of these materials to take up metal ions from aqueous solution has been briefly investigated.

1. Introduction

Insoluble ligands bearing chelating groups have potential application for the extraction and recovery of metals from solution. Given appropriate ligand groups, such extraction might even be selective. The advantage of solid ligands over their conventional soluble counterparts is principally one of convenience; contact with a metal-containing solution can be achieved batchwise or continuously without involving other solvents, so that long-term contact is possible. Provided the formation constants of the complexes involved are adequate, concentration of metals from solutions of very high dilution becomes possible. The advantages of solid ligands based on polysiloxanes have been discussed in earlier parts of this series [1–3], in which we have also described simple systems containing monodentate amines or phosphines or a bidentate amine. We now examine the incorporation of bis(2-aminoethyl)amine (dien) units and some derivatives.

2. Experimental section

Analytical data for the various polymer products described are collected in Table 1.

2.1. 3-Iodopropyltrimethoxysilane

To a solution of sodium iodide (76.8 g, 0.5 mol) in dry acetone (500 cm^3) 3-chloropropyltrimethoxysilane (97.8 g, 0.49 mol) was added dropwise. The mixture was then refluxed for 24 h, solvent was removed under vacuum and the residue extracted with diethyl ether (4 × 100 cm^3). The solvent was removed from the combined extracts and the residue distilled (b.p. 96–98°C/10 mmHg). Found: C, 24.5; H, 5.2; I 43.75; Cl, 0.3; calculated: C, 24.5; H, 5.3; I 43.40; Cl 0.0%.

2.2. 3-Halogenopropyl-functionalised polymers

Tetraethylorthosilicate and 3-chloro- or iodo-propyltrimethoxysilane were mixed in appropriate ratio in dry methanol, and hydrochloric acid was added as catalyst [*e.g.* $Si(OEt)_4$, 20 g, 96 mmol; $(MeO)_3Si(CH_2)_3Cl$, 9.51 g, 48 mmol; MeOH, 50 cm^3; HCl, 0.42 mol dm^{-3}, 4.75 cm^3]. The mixture was allowed to solidify overnight and then crushed, ground, dried at 100°C, washed with methanol (Soxhlet extraction), water and ether.

2.3. Iodide-exchanged polymers

The polymer (10 g) was suspended in dry acetone (500 cm^3) containing sodium iodide (37.5 g) and the mixture refluxed for 60 h. The solid was then filtered off, washed with water, methanol and ether, and dried *in vacuo* at 100°C. Halogen analysis: Cl, 7.4; I, 23.7% (mol ratio, 0.21 : 0.19).

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2.4. Functionalisation with diethylenetriamine and its Schiff bases

Bis(2-ethylbenzaldeneimine)amine (46 g) was dissolved in dimethylformamide (250 cm^3) and the 3-halopropyl-siloxane polymer (9 g) and sodium bicarbonate (10 g) were added. The mixture was heated at 110°C with stirring for 96 h, after which the solid was filtered off, washed with water, methanol and ether, and Soxhlet extracted with methanol until the solvent remained clear. Yield, 9.2 g.

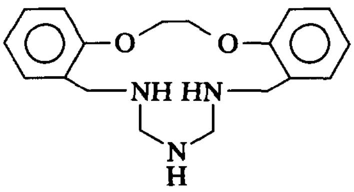
The salicylaldehyde-Schiff base ligand was prepared analogously. The Schiff base ligands were hydrolysed by reaction with HCl (6 mol dm^{-3}, 200 cm^3) at 60°C for 4 h. The solid was filtered off and washed with water, excess of NaOH (0.05 mol dm^{-3}) and water, until neutral. Yield, 6.5 g.

2.5. 2-Benzylaminoethylamine ligand

Benzaldehyde (62 g, 0.58 mol) was added to a solution of $(MeO)_3Si(CH_2)_3NH(CH_2)_2NH_2$ (130 g, 0.58 mol) in dry ethanol. When reaction was complete, $Si(OEt)_4$ (121.8 g, 0.58 mol) and water (21.3 g, 1.18 mol) were added and the mixture allowed to solidify overnight. The solid was crushed and washed with water, methanol and ether and dried *in vacuo* at 100°C. Yield, 200 g. A portion of this material (15 g) was reduced with sodium borohydride in methanol.

2.6. Macrocyclic ligand

The macrocycle **M** was prepared by the method used by Lindoy [4]. 1,2-dibromoethane (37 g, 0.20 mol) was refluxed with salicylaldehyde (49 g, 0.40 mol) and sodium hydroxide (16 g, 0.40 mol) in dry ethanol for 92 h. The precipitate of 1,4-bis(2′-formylphenyl)-1,4-dioxabutane was filtered off, washed with water and recrystallised from ether/chloroform. Yield, 20 g, 37%. Found: C, 71.3; H, 5.4; calculated: C, 71.1; H, 5.22%.



(M)

To this product (13.5 g, 50 mmol) in boiling methanol (700 cm^3) was added slowly 2,2′-diminodiethylamine (5.15 g, 50 mmol), boiling was continued for 30 min and the mixture was filtered and allowed to cool. Sodium tetrahydroborate (8.0 g, 0.22 mol) was added slowly and the total volume reduced to 150 cm^3. The mixture was cooled and water (400 cm^3) was added. An oil separated which was extracted by chloroform (4 × 100 cm^3). The combined extracts were dried (Na_2SO_4) and concentrated to 50 cm^3. Diethyl ether was added slowly, yielding a white solid, which was recrystallised from chloroform/ether. Found: C, 68.6; H, 7.7; N, 11.4; calculated: C, 70.5; H, 7.6; N, 12.1%.

The siloxane polymer prepared from $Si(OEt)_4$ and $(MeO)_3Si(CH_2)_3I$ (1 : 1, 5 g, 7.1 mmol total halogen) was treated with the macrocycle (4 g, 12 mmol) in DMF, and maintained at 100°C for 48 h under nitrogen. The resulting solid was filtered off, washed with water and ethanol, and dried at 80°C *in vacuo*.

2.7. Metal uptake

A known amount of the solid ligand was shaken with a solution containing a two-fold excess of the appropriate metal ion (usually as chloride). When necessary a citrate buffer was employed. Samples of the solution (70 μl) were removed periodically and analysed by atomic absorption.

TABLE 1. Analytical data

	Synthesis [a]	%C	%H	%N	%Hal
1(Cl)	TEOS + TM-Cl (1 : 1)	14.3	3.5		15.4 (Cl)
2(Cl)	TEOS + TM-Cl (2 : 1)	10.3	3.5		10.7 (Cl)
1(I)	1(Cl) + NaI				8.69 (Cl), 23.7 (I)
2(I)	2(Cl) + NaI				7.4 (Cl), 9.3 (I)
3(I)	TEOS + TM-I (1 : 1)	10.5	3.5		2.0 (Cl), 38.0 (I)
A	1(I) + dien-sal; hydrol	23.0	6.0	11.4	2.2
B	3(I) + dien-bz; hydrol	21.5	5.7	8.3	
C	3(I) + dien-bz	43.2	5.5	7.7	0.6 (Cl)
D	TEOS + TM-enbz (1 : 1), BH_4^-	45.9	5.8	8.8	
E	3(I) + macrocycle	21.6	6.3	2.5	1.4 (Cl), 6.2 (I)

[a] TEOS = $Si(OEt)_4$; TM–*Y* = $(MeO)_3Si(CH_2)_3Y$ [*Y* = Cl, I, enbz (= 2-benzoaminoethylamine); dien-sal = di-salicylaldehyde Schiff base of dien; dien-bz = di-benzaldehyde Schiff base of dien.

3. Results and discussion

There are essentially two methods for the preparation of functionalised, cross-linked siloxane polymers. Both involve the hydrolytic condensation of $Si(OEt)_4$ and $RSi(OR')_3$ (R' = Me, Et; R = a functionalised alkyl group), the difference lying in whether the ligand group is introduced into the group R before or after the polymerisation. For instance, trialkoxysilanes with R = 3-aminopropyl or 3-(2-aminoethyl)aminopropyl are commercially available. Other functionalised starting materials could be prepared by, for instance, replacement of the organochlorine group in $X_3Si(CH_2)_3Cl$ (X = Cl or OMe), provided that the reactions could be carried out under anhydrous conditions and the product could be separated and purified. These requirements are not trivial, and in the main we have preferred to prepare polymers containing 3-chloropropyl groups [from $Si(OEt)_4$ and $(MeO)_3Si(CH_2)_3Cl$] and to introduce the ligand groups in a second stage.

3.1. Preparation of initial polymer

For the hydrolytic condensation of $Si(OEt)_4$ and $(MeO)_3SiR$, when R is 3-chloropropyl, a catalyst is required. Previously we employed $Bu_2Sn(OAc)_2$ which leads to the incorporation of Bu_2Sn-groups in the resultant polymer [2,3]. This result has been confirmed during the present work, and led to the search for alternative catalysts. When R contains one or more amine groups these function as integral basic catalysts, and condensation and polymerisation occur smoothly without the need for any additional catalyst. The use of aqueous base (sodium hydroxide) leads to extremely rapid gelation which is not easily controlled, and the chlorine-content of the products is very low. This latter observation suggests that condensation may not be uniform and good cross-linking may not be established. On the other hand, catalysis by hydrochloric acid gives slow (hours) gelation and reproducible polymer formation. A series of experiments established that the most satisfactory mole ratio of HCl to $Si(OEt)_4$ was 0.1 : 1. A further advantage of this catalyst is that the polymers obtained show greater mechanical strength than those obtained with the dibutyltin catalyst: they are much less prone to degradation of the particles by mechanical and magnetic stirrers. This is presumably a result of the greater degree of chain entanglement and cross-linking which is established under slow acid-catalysed conditions [4].

The composition of the resulting polymers was reproducible to about 2%. However, as previously noted, the compositions did not correspond exactly to those of the reaction mixtures, suggesting some loss of oligomers formed by self-condensation of $(MeO)_3SiR$. The yields of only *ca.* 80% confirm this suggestion. It was, however, found possible with the HCl catalyst to obtain stable polymers from 1 : 1 mixtures of $Si(OEt)_4$ and $(MeO)_3SiR$ [*e.g.* **1**(Cl)]; such polymers have, of course, a higher content of the organic functional group. When this ratio was used with amine-containing R-groups (and no additional catalyst), the reaction mixtures always gave products which were readily soluble in water [2,5].

The porosity of **2**(Cl) was measured by the mercury-intrusion method, which showed an average pore diameter of 67 Å (median 72 Å), with the majority (*ca.* 80%) of pores having a diameter less than 200 Å.

The R = 3-chloropropyl polymers are stable to heating in air, losing less than 2.5% of weight at a constant 200°C. TGA studies showed that **1**(Cl) (prepared from 1 : 1 ratio of starting materials) lost only 1.2% up to 300°C (heating rate 5°C min^{-1}); above this temperature, considerable weight loss occurs, presumably due to oxidation. Polymer **2**(Cl) (2 : 1) loses 3.3% up to 300°C and oxidises thereafter. The loss in weight at moderate temperatures is presumably due to loss of adsorbed water and to elimination of water by condensation of residual hydroxy groups.

The polymers are also stable to acid, showing no loss in weight when washed repeatedly with hydrochloric acid (6 mol dm^{-3}). No dissolution is observed up to pH 11, but at pH 13 the polymer becomes sticky and begins to dissolve.

In the functionalisation reactions described below, it became necessary to replace the chlorine atoms of the 3-chloropropyl groups by iodine. This was achieved by reaction either of the preformed polymer or its precursor with sodium iodide in acetone. The former procedure resulted in about 50% replacement in **1**(Cl) and 23% in **2**(Cl), while direct reaction with $(MeO)_3Si(CH_2)_3Cl$ gave a crude product with 85% replacement (polymers **1**(I), **2**(I), **3**(I) respectively).

3.2. Introduction of ligand groups

3.2.1. Diethylenetriamine

Bis(2-aminoethyl)amine (= diethylenetriamine = dien) has been used as a chelating ligand for many decades. In principle it could be introduced into the present polymers by direct reaction with the 3-chloropropyl groups. However, such reactions are likely to lead to complicated cross-linking and cyclisation by reaction of both the primary and secondary amine groups. Such products would contain mixtures of ligand groups, some of which would have lost their chelating capacity. We therefore decided to employ the strategy used by Suzuki and Yokoyoma to introduce these ligand groups into chlorinated polystyrene [7]. The primary amine groups are protected by formation of a Schiff base with salicylaldehyde. On heating the polymers with the di-Schiff base in DMF at 100–110°C only about 20% replacement of the chlorine groups occurred. Similar results were obtained with the benzaldehyde Schiff base. The low degree of reaction is difficult to understand, since molecular models suggest that the effective diameter of the Schiff bases would be 12–17 Å, considerably smaller than the average pore size (*ca.* 70 Å). The iodide-exchange results (see above) suggest that the chlorine atoms in **1**(Cl) are more accessible than those in **2**(Cl). There should therefore be no problem of access of the Schiff bases to the potential reaction sites. We can only surmise that the groups bound initially block the entrance of further groups or that the C–Cl bond was not sufficiently active.

Reaction of the Schiff bases with 3-iodopropyl-functionalised polymers gave better incorporation of the ligand. A sample of **1**(Cl) was reacted with sodium iodide to give about 50% replacement of chlorine by iodine. Subsequent reaction with the benzaldehyde Schiff base gave about 80% reaction and all the remaining halogen was chlorine. This suggests that the iodide displaced has effectively catalysed reaction of residual chloro groups. Hydrolysis of this product with hydrochloric acid (6 mol dm^{-3}), followed by washing with dilute (0.05 mol dm^{-3}) alkali gave a material with lower nitrogen content than expected. Evidently, some of the functional groups were lost during this treatment, but whether this occurred by simple dissolution or represented some degradation of the polymer is not known. This product was investigated further (see below, ligand **A**).

The iodinated 1:1 starting polymer (I:Cl = 84:16) was then prepared by prior treatment of $(MeO)_3Si(CH_2)_3Cl$ with sodium iodide. Reaction with the benzaldehyde Schiff base resulted in about 90% replacement of halogen; the product contained only 0.6% Cl. Removal of the protecting group again resulted in some loss of the amine, the final composition being very similar to that of the previous product (this is referred to as ligand **B** below). Use of the salicylaldehyde Schiff base resulted in a final product containing rather less amine. The salicylaldehyde-Schiff base functionalised polymer was also used as a ligand (ligand **C**).

3.2.2. 2-Benzylaminoethylamine

The benzaldehyde Schiff base of $(MeO)_3Si(CH_2)_3NH(CH_2)_2NH_2$ was formed, polymerised with $Si(OEt)_4$ (1:1, without catalyst) and the resulting material reduced with sodium borohydride. The final product (ligand **D**) had a composition very close to that expected.

3.2.3. Macrocycle

The macrocyclic ligand **M**, 1,12,15-triaza-3,4,9,10-dibenzo-5,8-dioxacycloheptadecane, was prepared by the method of Lindoy *et al.* [4] and allowed to react with the 3-iodopropyl polymer in the presence of sodium bicarbonate. Analysis showed that about 30% of the total halogen had been replaced (ligand **E**).

3.3. Stability of ligands in water

A ligand prepared by the hydrolytic condensation of $Si(OEt)_4$ and $(MeO)_3Si(CH_2)_3NH_2$ (1:1), on treatment with copper(II) solution, gave considerable enhancement of the colour of the aqueous solution, suggesting the loss of copper-complexed oligomers. This behaviour continued through several washing, drying and re-use cycles, suggesting progressive degradation of the polymer. It was found that the leaching effect was most marked for samples of the polymer which had been stored and that it occurred also for diethylenetriamine-functionalised polymers. However, the benzaldehyde Schiff base was stable to storage and to exposure to water.

The most probable cause of this phenomenon is catalysis by the amine groups of the hydrolysis of the Si–O–Si bonds in the polymers, coupled with the formation of oligomers based on $(-O)_3Si(CH_2)_3NH_2$ units. The hydrolysis of $(MeO)_3Si(CH_2)_3NH_2$ is well-known to give water-soluble oligomers. Presumably the amine groups are sufficiently mobile, even in the solid material, to be able to attack neighbouring silicon atoms. Schiff-base formation removes the primary amine groups and replaces them by a much bulkier group, both of which would inhibit the attack. As a simpler way of achieving stability for amine-functionalised siloxane polymers, we recommend that they be stored as hydrochlorides.

3.4. Metal-uptake studies

Five of the solid ligands were selected for examination of their metal-uptake potential: **A** and **B**, with diethylenetriamine functional groups; **C**, the salicylaldehyde Schiff base of **B**; **D**, the hydrogenated benzaldehyde Schiff base of ethylenediamine; **E** the macrocycle.

3.4.1. Batch method

The saturation-capacities of the ligands were determined by shaking a known amount of the ligand with an unbuffered solution containing a known excess of copper(II) ion. The amount of copper remaining in solution after 24 h was measured (Table 2).

For ligands **A** and **B**, 1:1 complexes are formed as would be expected for tridentate ligands. The Schiff base ligand **C** showed a much lower uptake of copper,

TABLE 2. Saturation capacities of solid ligands

Ligand	Metal capacity/mmol g^{-1}			Ligand content/ mmol g^{-1}
	Cu^{2+}	Ni^{2+}	Co^{2+}	
A (dien)	2.00	1.1	0.60	1.84
B (dien)	2.14	0.97	0.63	1.98
C (dien-bz)	0.34	0.10	0.11	1.02
D (enbz)	2.07	0.031	0.024	3.10
E (macro)	0.22			0.59

which may be due to its hydrophobic nature—the solid ligand is very poorly wetted by water. Ligand **D** is a bidentate; saturation with metal might give 1:1 complexes, but the thermodynamic advantage of forming 2:1 complexes might be overwhelming, if the ligands were suitably placed. The data suggest that approximately half the metal is bound in this manner, the rest in 1:1 complexes. This behaviour is similar to that of the simple ethylenediamine ligand investigated previously [1]. The macrocyclic ligand, **E**, took up only about half the expected amount of copper. Since the ligand groups must be close to the surface, this may again indicate poor wetting or that insufficient time was allowed.

The rate of uptake of copper by the ligands was investigated. In unbuffered solution uptake by **A** was very rapid, reaching saturation within 15 min. Ligand **B** was somewhat slower, achieving 50% of saturation capacity in 60 min, and more than 90% in 200 min. This difference is not readily explicable. Both ligands were prepared by functionalization of a preformed polymer and both have similar average concentrations of ligand groups. The only difference lies in the preparation of the initial polymer, since **A** was prepared by iodide-exchange from the chloropropyl polymer and **B** by iodide-exchange before polymerisation. It would not be expected that the polymerisation-condensation reactions of chloro- and iodo-propyltrimethoxysilane would give products of greatly different structure.

Both **C** and **D** reacted considerably more slowly, reaching about 50% of capacity in 270 and 420 min respectively.

An interruption test [8] was performed with **A**. That is, the ligand was separated from the solution after a few minutes, when the rate of uptake was beginning to diminish, and then replaced. The rate of uptake increased, indicating that the limiting factor is diffusion of metal ions into the ligand particles. Such diffusion continues during the separation period, liberating some surface sites for rapid metal uptake when the ligand is replaced in the solution.

It was noted that the pH of the copper solution increased as the metal ion was absorbed, and an attempt was made to use buffered solutions. At pH 2 and 4, in citrate buffer, the rate of copper-uptake was reduced considerably, although the final saturation values were similar. This behaviour is presumably due to the formation of citrate complexes which inhibited the binding of copper to the triamine ligand.

Uptake of nickel(II) and cobalt(II) was also measured in unbuffered solution (Table 2). Ligands **A** and **B** appeared to form 2:1 complexes with nickel(II), which is consistent with its normal readiness to form octahedral complexes. The lower uptake of cobalt(II) may be a reflection of the need for a slightly higher pH for optimum complexation of this metal ion. Ligand **C** again suffers from hydrophobicity, but **D** displays considerable selectivity, taking up only a few percent of the amount of copper absorbed by the same ligand.

3.4.2. Column experiments

A short column of ligand **A** was prepared and buffered to pH 3.5 (acetate buffer). On passing a copper(II) solution, breakthrough occurred at a loading of 0.30 mmol (Cu^{2+}) g^{-1}. At pH 4.5 and 5.0, the breakthrough capacities were 0.93 and 1.25 mmol g^{-1} respectively. Even the highest value is only about 65% of the saturation value obtained by the batch method, suggesting that the lower parts of the column had not had time to reach saturation. The column could be re-used by washing with hydrochloric acid (0.1 mol dm^{-3}) and re-equilibrating with buffer.

Breakthrough capacities of 0.16 and 0.31 mmol g^{-1} of nickel(II) were found at pH 5.5 and 7.0, and 0.18 mmol g^{-1} of cobalt(II) at pH 7.6. On washing with acid some cobalt remained on the column as a pink band which could not be removed even with 3 mol dm^{-3} acid, suggesting that oxidation to cobalt(III) had occurred. When a mixture of cobalt(II) and nickel(II) was applied at pH 7, only the nickel was retained.

4. Conclusion

The functionalisation of polysiloxane polymers with ligand groups gives materials which are rigid and have good thermal and hydrolytic stability. A simple method of functionalisation is by reaction of amines with pendant 3-chloropropyl groups. Although not all the 3-chloropropyl groups react, this procedure has the advantage that ligand groups are placed in the most accessible positions. Groups located deep in narrow pores do not react, but replacement is optimised by prior reaction with sodium iodide. A variety of chelating ligand groups can be introduced in this way (the use of glycinate and iminodiacetate groups will be described in a forthcoming paper [9]). These materials can be employed to extract metal ions from aqueous solution, or as chromatographic stationary phases to separate metal ions. They can also be used in organic solvents without swelling.

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