

## **Insoluble ligands and their applications**

### **I. A comparison of silica-immobilized ligands and functionalized polysiloxanes**

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#### **Abstract**

Insoluble amine and diamine ligands have been prepared by two routes: by immobilisation of the compounds  $(\text{MeO})_3\text{Si}(\text{CH}_2)_3\text{E}$  ( $\text{E} = \text{NH}_2$  or  $\text{NH}(\text{CH}_2)_2\text{NH}_2$ ) on silica, and by the incorporation of these compounds into a siloxane polymer by co-hydrolysis with  $\text{Si}(\text{OEt})_4$ . The latter gives robust materials with a higher content of available ligand groups than their immobilized counterparts, as measured by the uptake of protons and of copper(II) ion. Preliminary examination has been made of the relative uptake of other metal ions by the propylamine-functionalized polymer.

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#### **Introduction**

There has been much interest in the use of ligands immobilized by grafting on to an insoluble support. In view of its high thermal stability and general chemical inertness, silica has often been chosen as the base matrix, and there have been two major applications of such materials. On the one hand, the ligands themselves have been used in the extraction of metals or in chromatography [1]. On the other, transition-metal complexes of the ligands have been used as catalysts in a variety of reactions [2,3]. In the catalysis of reactions such as hydrosilylation, leaching of the active metal into solution is sometimes a problem [4,5], and we have demonstrated that, in one case at least, this involves cleavage of the ligand from the surface [4]. In order to prevent this problem, which limits the effective re-use of the catalyst, we are developing a range of versatile ligands prepared by the hydrolytic condensation of suitably functionalized alkoxy silanes, in which the ligand groups form an integral part of the resulting insoluble polysiloxane. Similar materials have been used to immobilize biological materials [6,7] and in chromatography [8], but there appears only to be a single report of their use in catalysis [9]. We intend to explore the utility

of these ligands in catalysis and also in the extraction of metals from solution. Brisdon has recently described the preparation of related soluble materials with low molecular weights [10].

In this paper we present a comparison between silica-immobilized ligands and their polysiloxane counterparts. In subsequent papers we shall describe applications of the polysiloxane ligands and their complexes.

## Experimental

Abbreviations for the starting materials are given in Table 1, and analytical data for the polymers in Table 2.

### Activation and OH-content of silica

Silica gel was activated by refluxing in concentrated hydrochloric acid for 4 h, washed with water until free of chloride, and dried at 320 °C [11].

Before determination of the OH-content [12], samples were repeatedly washed with anhydrous diethyl ether. The final washings were tested for the presence of water by the addition of a Grignard reagent, methylmagnesium iodide. Samples of the silica (ca. 200 mg) were then treated with an excess of methylmagnesium iodide in ether; when evolution of methane had subsided, the mixture was refluxed for 10–15 min. The solid was separated and washed free of Grignard reagent with ether. After drying at 50–60 °C, the sample was weighed and treated with hydrochloric acid (20 cm<sup>2</sup>, 1.0%), and the mixture was evaporated to small bulk. The solid was filtered off and washed with hot HCl to extract the bound magnesium. The

Table 1  
Ligands anchored and mole ratios of products

Ligand	C/Y <sup>a</sup>
(EtO) <sub>3</sub> Si(CH <sub>2</sub> ) <sub>3</sub> NH <sub>2</sub> (I)	3.1(3.0)
(EtO) <sub>2</sub> SiMe(CH <sub>2</sub> ) <sub>3</sub> NH <sub>2</sub> (II)	6.4(4.0)
(MeO) <sub>3</sub> Si(CH <sub>2</sub> ) <sub>3</sub> NH(CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub> (III)	2.6(2.5)
Cl <sub>3</sub> Si(CH <sub>2</sub> ) <sub>3</sub> Cl (IV)	3.9(3.0)
Cl <sub>2</sub> SiMe(CH <sub>2</sub> ) <sub>3</sub> Cl (V)	4.8(4.0)
(MeO) <sub>3</sub> Si(CH <sub>2</sub> ) <sub>3</sub> Cl (VI)	3.9(3.0)
(MeO) <sub>3</sub> Si(CH <sub>2</sub> ) <sub>3</sub> SH (VII)	3.7(3.0)

<sup>a</sup> Y = N, Cl, or S. Figures given are mole ratios (calculated value).

Table 2  
Analytical data for polysiloxanes

Siloxane	Functional group	%C	%H	%Y <sup>a</sup>	mmol (X) g <sup>-1</sup> <sup>b</sup>	C/Y <sup>c</sup>
A	(CH <sub>2</sub> ) <sub>3</sub> NH <sub>2</sub>	11.9	3.8	4.6	3.06(3.28)	3.0(3.0)
B	(CH <sub>2</sub> ) <sub>3</sub> NH(CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub>	14.3	5.4	7.1	4.95(5.07)	2.3(2.5)
C	(CH <sub>2</sub> ) <sub>3</sub> Cl	17.9	4.4	10.7	2.96(3.01)	4.9(3.0)
D	(CH <sub>2</sub> ) <sub>3</sub> SH	15.4	3.7	10.9		3.8(3.0)

<sup>a</sup> Y = N, Cl, or S. <sup>b</sup> Found by H<sup>+</sup>-uptake or Volhard determination. Values in parentheses are calculated from the microanalytical figure. <sup>c</sup> Mole ratio. Figures in parentheses are the theoretical values.

Table 3

Proton-uptake for polymeric and silica-supported amine ligands

Ratio Si(OEt) <sub>4</sub> /I	H <sup>+</sup> -uptake (mmol (H <sup>+</sup> ) g <sup>-1</sup> )	Ratio Si(OEt) <sub>4</sub> /III	H <sup>+</sup> -uptake (mmol (H <sup>+</sup> ) g <sup>-1</sup> )
3/1	2.50	3.0/1	4.09
2/1	3.05	2.5/1	4.50
1/1	1.97	2.0/1	4.95
1/2	1.46	1.5/1	4.48
1/3	0.78		
SiO <sub>2</sub> -I	1.05	SiO <sub>2</sub> -II	1.91

combined filtrate and washings were titrated with EDTA under standard conditions [13]. The average OH-content was found to be 5.2 mmol g<sup>-1</sup> (Aldrich chromatographic silica, 60–120 mesh) or 5.2 mmol g<sup>-1</sup> (Fisons, 60–120 mesh).

#### *Silica-supported aminopropanes (SiO<sub>2</sub>-I, -II, and -III)*

SiO<sub>2</sub>-I was prepared by refluxing activated silica gel (10 g) with I (3.1 g, 14 mmol) in dry toluene (65 cm<sup>3</sup>) for 4 h. The solid was filtered off, washed with toluene, then methanol, and dried at 100 °C. Found: C, 4.3; H, 2.8; N, 1.6%.

SiO<sub>2</sub>-II and -III were prepared analogously. Found: C, 3.3; H, 1.0; N, 0.6; C, 6.6; H, 2.1; N, 2.9%, respectively.

#### *Polysiloxanes A and B*

Polysiloxane A was prepared by stirring tetraethoxysilane (20 g, 96 mmol) and water (4.75 g, 260 mmol) together in an ice-bath for 5 min, after which I (10.6 g, 48 mmol) was added. After a few minutes' further stirring, the mixture solidified. It was crushed, allowed to stand at room temperature for several hours, and dried overnight at 100 °C. The solid was sieved, washed with water, and dried at 100 °C. Yield, 10.5 g.

Polysiloxane B was prepared analogously from Si(OEt)<sub>4</sub> and III, except that about 2 h at room temperature were required for solidification of the mixture.

#### *Polysiloxanes C and D*

Polysiloxane C was obtained by adding water (4.75 g, 260 mmol) and methanol

Table 4

H<sup>+</sup>- and Cu<sup>2+</sup>-uptake

Ligand	H <sup>+</sup> -uptake (mmol g <sup>-1</sup> ) <sup>a</sup>			Cu <sup>2+</sup> -uptake (mmol g <sup>-1</sup> ) <sup>b</sup>		
	2 h	15 h	24 h	2 h	15 h	24 h
SiO <sub>2</sub> -I	0.87(76)	1.04(91)	1.05(93)	0.42(74)	0.52(91)	0.56(98)
SiO <sub>2</sub> -III	1.60(77)	1.93(93)	1.91(92)	0.44(43)	0.81(78)	0.82(79)
A	2.54(77)	3.03(92)	3.06(93)	1.35(82)	1.50(91)	1.50(91)
B	3.80(75)	4.93(97)	4.95(98)	1.46(58)	2.44(96)	2.45(97)

<sup>a</sup> Figures in parentheses are percentages of the theoretical maximum, calculated from the percentage of available nitrogen. <sup>b</sup> Figures in parentheses are percentages of the theoretical maximum, calculated assuming two nitrogen atoms bind to one copper atom.

(15 cm<sup>3</sup>) to Si(OEt)<sub>4</sub> (20 g, 96 mmol). The mixture was stirred and VI (9.53 g, 48 mmol) and Bu<sub>2</sub>Sn(OAc)<sub>2</sub> (1.0 g, 3 mmol) were added. Solidification occurred after a few hours. The solid was treated as above.

Siloxane **D** was prepared analogously from Si(OEt)<sub>4</sub> and VII.

#### *Metal-uptake*

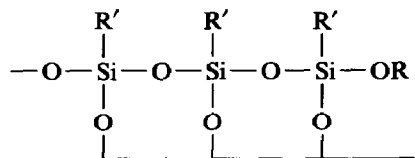
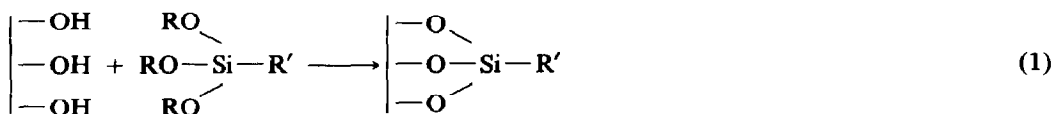
The solid ligand (ca. 300 mg) was stirred with a solution of the metal ion (25 cm<sup>3</sup>, 0.1 mol dm<sup>-3</sup>) for the required time, separated by filtration, and washed with water. The residual metal ion in the filtrate and washings was determined by atomic absorption or by EDTA titration. Proton-uptake was determined analogously. Data are given in Tables 3 and 4.

## Results

#### *Silica-immobilized ligands*

Silica gel was activated by treatment with 35% hydrochloric acid [11]. The hydroxyl-content of the silica after drying at 325 °C was determined by reaction with a Grignard reagent [12]. Reactions with 3-aminopropyltriethoxysilane, I (see Table 1), were carried out at various mole ratios of I/Si-OH, and the products were washed with water and then with hydrochloric acid (0.1 mol dm<sup>-3</sup>). Analysis of the products before and after washing showed that loss of ligand occurred during washing at all ratios above 1/10, and that the losses occurred primarily in the water-wash. All materials were therefore thoroughly washed with water before use. The materials removed are presumably oligomeric siloxanes produced by self-condensation reactions; such oligomers are known to be water-soluble (see below).

Similar reactions were conducted with a variety of functionalized alkoxy- and chloro-silanes (Table 1). In all cases, analysis of the products showed C/X ratios (X = N, Cl or S) slightly higher than expected for complete removal of the alkoxy groups (Table 1). These results are consistent with those of previous workers who showed that the anchoring reaction is not the simple process of eqn. 1, but involves a combination of condensative-oligomerisation and reaction with the silica to give products of type VIII [14]. There is also the possibility that some of the OH-groups on the silica surface react with the alcohol liberated to give surface alkoxy-groups. In each case there is a small proportion of residual alkoxy-groups, which raises the carbon-content.



(VIII)

The materials obtained from anchoring silanes containing 3-chloropropyl-groups (IV-VI) to silica lend themselves to the preparation of a wide range of further

ligands by functionalization of the organic group, for example, by reaction with amines: we have investigated piperidine, morpholine, and pyrrolidine.

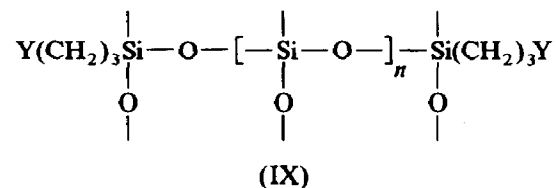
All the amine-containing materials complex with a variety of cations in neutral aqueous solution:  $\text{Ag}^+$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{UO}_2^{2+}$ ,  $\text{Al}^{3+}$ . Binding can be reversed by treatment with dilute acid (e.g.  $0.1 \text{ mol dm}^{-3} \text{ HCl}$ ). In the case of  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$ , however, some of the metal is retained as brown/orange bands; this is presumably due to aerial oxidation which would be enhanced by the high local basicity within the ligand. Ligand  $\text{SiO}_2$ -VII shows preference for heavy metals, such as  $\text{Hg}^{2+}$  and  $\text{Pd}^{2+}$ . No doubt the ligands could be used for the extraction and/or separation of metals from solution but, in view of the general superiority of the polysiloxane ligands described below, we have investigated only  $\text{SiO}_2$ -I and  $\text{SiO}_2$ -II. Data for these systems is given later, in order to compare them with their polysiloxane analogues.

### Polysiloxane ligands

When I is hydrolyzed alone, the resulting mixture of oligomers is completely water-soluble. Further condensation and cross-linking can be achieved by the addition of tetraethoxysilane to the hydrolysing mix. Several different ratios of reactants were investigated, and the products were assayed by determination of their  $\text{H}^+$ -uptake, as a measure of the proportion of available amine-groups (Table 2). Analytical data confirm that these account for more than 90% of the total nitrogen present (see Table 4).

The optimum ratio of  $\text{Si}(\text{OEt})_4/\text{I}$  is 2/1. Below this there is considerable formation of amine-containing oligomers, which are lost during washing. Above 2/1, little material is lost by washing but, of necessity, the proportion of amine present is lower. The product from the 2/1 ratio (designated A) was selected for further study. Similar results were obtained for the co-condensation of  $\text{Si}(\text{OEt})_4$  and III (Table 2). Again, the 2/1-product (B) was selected for evaluation.

Condensation reactions were also carried out with 2/1 ratios of  $\text{Si}(\text{OEt})_4$  and VI (to give C) and with VII (D). In these cases, since the organic group was not basic, it was necessary to add dibutyl-tin diacetate as catalyst.



From the stoichiometry of the reaction mixtures, the simplest possible structure for the polysiloxanes would be the two-dimensional ladder, IX ( $\text{Y} = \text{NH}_2$ ,  $\text{NH}(\text{CH}_2)_2\text{NH}_2$ ,  $\text{Cl}$ , or  $\text{SH}$ ), with  $n = 4$ . Siloxanes A and B have C/N ratios identical to those expected, within experimental error (Table 3), but the absolute amounts of these elements are less than calculated for IX ( $n = 4$ ). The composition of A corresponds to that for  $n = \text{ca. } 6.5$ , and that of B to  $n = \text{ca. } 8.4$ . Clearly, these are average values, but they indicate that during the condensation process the amine-silanes I and III have undergone some oligomerisation as well as cross-linking. The oligomers have been lost in washing, resulting in an increase in the proportion of 'backbone'  $\text{SiO}_4$ -groups. The organic functional group may also be

playing a rôle in determining the structure and, hence, the stoichiometry of the polymer. The actual structure is undoubtedly more complex than IX, and is probably a porous three-dimensional framework.

Siloxanes C and D have higher C/Y ratios (Y = Cl or S) than expected. The absolute carbon content is also higher than expected for IX ( $n = 4$ ), but the Y-content is lower. Two possible explanations suggest themselves for this behaviour. First, hydrolysis may have been incomplete, leaving some residual methoxy groups. Alternatively, and more probably, some  $\text{Bu}_2\text{Sn}$ -groups, originating from the catalyst, may have been incorporated in the solid; even with the relatively small amounts of catalyst employed (2% relative to total silicon), its retention would significantly increase the carbon content of the polymer. We have NMR and Mössbauer spectroscopic evidence from related systems that such incorporation does occur [15]. The analytical data again suggest loss of some oligomers during the polymerisation/washing process ( $n = 5, 6$ ).

#### *Proton- and metal-uptake*

The proton-uptake of ligands A and B and  $\text{SiO}_2$ -I and -III were compared by stirring the ligand with an excess of dilute acid ( $0.1 \text{ mol dm}^{-3}$ ) for various times. In all cases, uptake increased between 2 and 15 h contact time, but did not change during the next 9 h (Table 4). This would seem to indicate that, even for ligands anchored on the surface of silica, not all the amine-sites are readily accessible. However, for all the ligands, more than 90% of the amine-groups became protonated when contact was prolonged. The polysiloxane ligands contain 2–3 times more available amine-groups per gram than the silica-supported ligands.

Similar trends were found in the reaction of the ligands with copper(II) in aqueous solution (at pH 5; see below for the pH-dependence studies). Saturation is again achieved within 15 h (Table 4). The stoichiometry suggests that, in all cases, each copper ion is bound to only two amine-groups, regardless of whether they

Table 5  
Spectroscopic data for copper complexes

Ligand	Absorption maxima	ESR
$\text{SiO}_2$ -I	720 nm ( $13900 \text{ cm}^{-1}$ )	$g_{\perp} 2.07, g_{\parallel} 2.28, A(^{65}\text{Cu}) 136 \times 10^{-4} \text{ cm}^{-1}$
A	715 nm ( $14000 \text{ cm}^{-1}$ )	
B	650 nm ( $15400 \text{ cm}^{-1}$ )	

Table 6  
Uptake of divalent metal ions by insoluble ligands

Ligand	Metal-uptake ( $\text{mmol g}^{-1}$ ) <sup>a</sup>		
	$\text{Cu}^{2+}$ (pH 5)	$\text{Co}^{2+}$ (pH 9)	$\text{Zn}^{2+}$ (pH 7)
$\text{SiO}_2$ -I	0.56 (1.9)	0.11 (9.5)	0.28 (3.8)
$\text{SiO}_2$ -II	0.79 (2.4)	0.36 (5.3)	0.58 (3.3)
A	1.50 (2.0)	0.40 (7.5)	0.60 (5.0)
B	2.46 (2.1)	0.72 (7.0)	1.59 (3.2)

<sup>a</sup> Figures in parentheses are mole ratios of available nitrogen to metal ion.

Table 7

Metal-uptake of siloxane A as a function of pH

pH	Uptake (mmol g <sup>-1</sup> ) <sup>a</sup>			
	Ni <sup>2+</sup>	Co <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>
3	0.05(13)		0.15(10)	
4	0.09(23)	0.03(10)	1.37(91)	0.07(12)
5	0.14(35)	0.16(53)	1.45(97)	0.15(25)
6	0.18(45)	0.20(67)	1.50(100)	0.38(63)
7	0.38(95)	0.28(93)	1.42(95)	0.60(100)
8	0.40(100)	0.29(97)		0.60(100)
9	0.31(76)	0.30(100)		0.45(75)

<sup>a</sup> Figures in parentheses are the uptake as a percentage of the maximum.

originate from separate propylamine-groups or a single diaminoethane-group. Four-co-ordination is presumably completed by two anions. UV-visible reflectance spectra and ESR spectra were obtained for the copper(II)-loaded ligands (Table 5), and are consistent with square-planar CuN<sub>2</sub>X<sub>2</sub>-co-ordination. The absorption maximum found for B-Cu<sup>2+</sup> is close to that reported for Cu(en)<sup>2+</sup> [16].

Cobalt(II) and zinc(II) are also readily taken up, and show a similar time-dependence. However, considerably less of these metals is bound (Table 6), even when the optimum pH for each is chosen. For siloxane A, the nickel content was also determined as 0.40 mmol g<sup>-1</sup>, i.e. similar to cobalt(II) and zinc(II) and considerably less than copper(II). These differences are presumably related to the different stereochemistries and co-ordination numbers preferentially adopted by these metal ions. Zinc(II) is likely to be tetrahedrally co-ordinated, and the uptake data suggest that this involves two amine groups. The lower uptake than for copper may be connected with the smaller bond angle required, or with the presumed irregularity of distribution of amine groups throughout the polymer matrix, or it may indicate that initial binding of the metal ion effectively blocks the access to deeper sites. Similar considerations apply to cobalt and nickel, except that these ions may be expected to be octahedrally co-ordinated, and may therefore bind to a larger number of amine groups.

A simple pH-study of the metal uptake of polysiloxane A was made with Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, and Zn<sup>2+</sup> (Table 7). As would be expected, Cu<sup>2+</sup> binds strongly at much lower pH than the other metals. Since the pH-scan was only rather coarse, it is not possible to distinguish the binding of the other metals, but it appears that the pH at which significant uptake begins increases from Ni<sup>2+</sup> to Co<sup>2+</sup> to Zn<sup>2+</sup>; these data will be refined at a later date.

## Conclusion

Secure immobilization of trialkoxysilyl-containing ligands on silica can be achieved provided the ratio of ligand to available hydroxyl groups on the surface is carefully controlled, e.g. -Si(OR)<sub>3</sub>/SiOH < 1/10. These materials are useful ligands, but those obtained by co-polymerisation of the trialkoxysilyl material with tetraethoxysilane give much higher proportions of functional groups. Both procedures appear to produce porous materials which require substantial contact times for

saturation with either metal ions or with protons. However, in the case of the siloxanes, the whole pore structure is evidently lined with functional groups, giving far higher uptakes than the supported ligands at comparable particle sizes. A wide range of functionalities is possible, either by direct synthesis, as illustrated above, or by further derivatization of materials such as siloxane C (3-chloropropyl functionalization). These polysiloxane ligands have potential in the extraction of metals and in the heterogenization of catalysts, and later papers in this series will illustrate these applications.

## References

- 1 D.E. Leyden in D.E. Leyden and W.T. Collins (Eds.), *Silylated Surfaces*. Gordon and Breach, New York, 1980, p. 333 and references therein.
- 2 L.L. Murrell in J.J. Burton and R.L. Garten (Eds.), *Advanced Materials in Catalysis*, Academic Press, New York, 1977, p. 236.
- 3 D.C. Bailey and S.H. Langer, *Chem. Rev.*, 81 (1981) 109.
- 4 R.V. Parish and M.I. Vania, *J. Organomet. Chem.*, 263 (1984) 139.
- 5 E.N. Ejike and R.V. Parish, *J. Organomet. Chem.*, 321 (1987) 135.
- 6 H. Karatami, H. Minakuchi, and S. Oka, *Nippon Kagaku Kaishi*, 11 (1983) 1577.
- 7 D.L. Venton, K.L. Cheesman, R.T. Chatterton, and T.L. Anderson, *Biochim. Biophys. Acta*, 797 (1984) 343.
- 8 K.K. Unger, N. Becker, and P. Roumeliotis, *J. Chromatogr.*, 125 (1976) 115.
- 9 F.G. Young, *Ger. Pat.*, (1974), 2,330,308 (CA 80, 121737f).
- 10 B.J. Brisdon and A.M. Watts, *J. Chem. Soc., Dalton Trans.*, (1985) 2191.
- 11 W.A. Aue and C.R. Hastings, *J. Chromatogr.*, 42 (1969) 319.
- 12 N.G. Roslayakova and V.B. Aleksovskii, *Zh. Prikl. Khim.*, 39 (1966) 795.
- 13 P.G. McMormick, *J. Chem. Educ.*, 42 (1973) 319.
- 14 T.G. Waddell, D.E. Leyden, and M.T. DeBello, *J. Amer. Chem. Soc.*, 103 (1981) 5303.
- 15 D. Habibi, V. Mohammadi and R.V. Parish, *J. Organomet. Chem.*, 369 (1989) 17.
- 16 L.W. Burgraaf, D.S. Kendall, D.E. Leyden, and F.J. Pern, *Anal. Chim. Acta*, 129 (1981) 19.