Journal of Organometallic Chemistry, 452 (1993) 19–22

JOM 23346

Insoluble ligands and their applications

III *. Polysiloxane diaminoethane derivatives

I.M. El-Nahhal [1] and R.V. Parish

Department of Chemistry, UMIST, Manchester M60 1QD (UK)

(Received October 7, 1992)

Abstract

Solid porous ligands containing bound diaminoethane groups have been prepared by hydrolytic condensation of $Si(OEt)_4$ with $(MeO)_3Si(CH_2)_3NH(CH_2)_2NH_2$. In aqueous solution, essentially all the ligand groups react with H_3O^+ ions, and a large proportion reacts with divalent metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}). EPR and visible spectra suggest that 1:1 and 2:1 complexes are formed. Preliminary data suggest that such materials have potential for ion-exchange.

1. Introduction

Ligands that are insoluble have many applications, as witnessed by the widespread use of materials based on functionalised polystyrene. However, polystyrene and other organic polymers suffer from defects such as variable degrees of swelling in solvents and limited thermal stability. Materials with an inorganic base are considerably better in both respects, and much work has been carried out with ligand groups grafted on to the surface of silica or other metal oxides [1–3]. We have preferred to use systems in which the ligand groups are bound to an inorganic polymer, such as a polysiloxane [4,5]. Such materials can, in principle at least, contain a much higher density of ligand groups than can be achieved by surface silylation, and the anchorage of the ligand groups is generally more secure. We describe now further investigation of systems in which $(CH_2)_3NH(CH_2)_2NH_2$ groups are incorporated in such polymers, and the characterisation of some metal complexes derived from them.

2. Experimental section

2.1. Preparation of ligands

The ligands were prepared by mixing tetraethoxysilane and vinyltrimethoxysilane in various ratios (see Table 1) with the calculated amount of water. The mixture was stirred for a few minutes and the required quantity of $(MeO)_3(CH_2)_3NH(CH_2)_2NH_2$ was added. Gelation occurred usually within a few minutes, and the product was then allowed to stand for several hours, dried overnight at 75°C *in vacuo*, crushed, sieved and washed with water, methanol and ether, and dried. The compositions of the mixtures used and the microanalytical data of the products are shown in Table 1.

2.2. Proton uptake

The solid ligand (250 mg) was shaken with hydrochloric acid (0.2 mol dm^{-3}, 30 cm^3) for three days. The solid was filtered off and washed with water, the washings were added to the filtrate and the whole was titrated with sodium hydroxide. The results are presented in Table 2.

2.3. Metal uptake

(a) Uptake *vs.* time: the solid ligand (500 mg) was shaken with an aqueous solution of copper(II) ion (0.1 mol dm^{-3}, 30 cm^3) and samples of the solution were

---

Correspondence to: Dr. R.V. Parish.

* For Part II, see ref. 5.

[1] Present address: Department of Chemistry, Islamic University of Gaza, PO Box 108, Gaza (via Israel).

0022-328X/93/$6.00

TABLE 1. Composition of polysiloxane ligands

Ligand	Molar ratios (I:II:III)	%C	%H	%N	C/N
A	2:0:1	20.1 (22.0)	5.0 (4.8)	8.7 (10.3)	2.7 (2.5)
B	1:0:1	23.2 (28.2)	6.6 (6.1)	10.9 (13.1)	2.5 (2.5)
C	1:1:1	26.6 (28.8)	5.9 (5.6)	8.1 (9.6)	3.8 (3.5)
D	4:1:1	15.6 (17.8)	3.3 (3.6)	5.0 (5.9)	3.1 (3.5)

Calculated elemental percentages (in parentheses) are based directly on the ratios of starting materials; I = $Si(OEt)_4$, II = $(MeO)_3SiCH=CH_2$, III = $(MeO)_3Si(CH_2)_3NH(CH_2)_2NH_2$.

TABLE 2. Proton uptake

Ligand	H^+ uptake (mmol g^{-1})	N content (mmol g^{-1})
A	5.8	6.2
B	7.0	7.8
C	5.7	5.8
D	3.6	3.5

TABLE 3. Copper(II) uptake *vs.* time (mmol (Cu) g^{-1})

Time (min)	A	B
10	0.074	0.93
20		1.36
50		1.68
60		1.96
120	0.21	
180		1.86
240	0.77	
300	0.85	1.73
1440	0.99	1.70

withdrawn periodically for AA analysis. Results are presented in Table 3.

(b) Saturation capacity: the ligand was shaken with a metal ion solution for three days, filtered off, washed with water, methanol and ether, dried and analysed directly. Results are presented in Table 4.

2.4. *Electron paramagnetic resonance*

In order to avoid relaxation effects due to over-high concentrations of metal ion, the ligands were first saturated with zinc(II) (as chloride) and then treated briefly with a solution of copper(II) chloride.

3. Results and discussion

Polymeric ligands were prepared by the hydrolytic condensation of mixtures of $Si(OEt)_4$, $(MeO)_3SiCH=CH_2$ and $(MeO)_3Si(CH_2)_3NH(CH_2)_2NH_2$. The amine functionalities act as excellent basic catalysts, and gelation occurs rapidly. The vinyl silane was included simply as a non-ligand diluent.

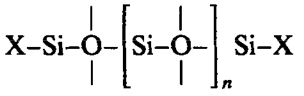
In a previous study [6], we attempted to prepare ligands of this type by condensing $Si(OEt)_4$ with $(EtO)_3Si(CH_2)_3Cl$ and subsequently reacting the chloropropyl group with 1,2-diaminoethane. Reaction occurred readily, but it was evident that there was considerable, non-reproducible cyclisation, by reaction of the two amine groups with adjacent chloropropyl groups.

The analytical data (C:N mole ratios, Table 1) indicate that hydrolysis was essentially complete; there is little residual alkoxy group present. The overall compositions indicate that the polymers correspond

TABLE 4. Analytical data for complexes of solid ligands

Ligand	Metal	%C	%H	%N	%M	N/M
A	Cu^{II}	17.5	4.4	8.6	4.4	8.9
	Ni^{II}	11.2	3.8	5.7	5.5	4.3
	Co^{II}	14.8	4.3	6.9	2.8	10.4
	Mn^{II}	17.3	4.8	7.3	2.1	13.7
B	Cu^{II}	20.4	4.6	10.2	7.6	6.1
	Ni^{II}	14.5	4.8	8.2	7.3	4.7
	Co^{II}	15.9	5.0	8.3	6.5	5.4
	Mn^{II}	17.4	3.6	6.6	5.6	4.6
C	Cu^{II}	17.7	4.5	6.8	5.1	6.1
	Ni^{II}	15.3	5.0	5.2	6.5	3.4
	Co^{II}	15.1	4.5	5.1	3.3	6.1
	Mn^{II}	20.8	5.2	5.8	5.4	4.2
D	Cu^{II}	14.2	3.5	5.9	3.2	8.4
	Ni^{II}	12.2	3.6	4.4	2.6	7.1
	Co^{II}	13.4	3.9	4.3	2.4	7.6
	Mn^{II}	12.9	3.3	4.0	1.5	10.5

reasonably closely to the formulae expected on the basis of the stoichiometry of the reaction mixtures, *i.e.* to ladder polymers of the type



$$\text{X-Si-O-}\left[\text{Si-O-}\right]_n\text{Si-X}$$

However, as observed previously [4], the absolute carbon contents are a little low suggesting that condensation is not uniform and that the trialkoxysilane components form small amounts of non-cross-linked oligomers which are lost during the washing process. It is well known that hydrolytic condensation of $(RO)_3SiR'$ leads to small, soluble polymers [7]. Equally, base catalysis tends to give polymers which are less interpenetrating or entangled [9]. The actual structure of the solids is not known but they are undoubtedly porous [8], three-dimensional, cross-linked polymers.

Reaction of the solid ligands with acid shows that effectively all the amine groups are accessible, at least to H_3O^+.

For two of the ligands the rate of uptake of copper(II) was determined, in order to define the time needed for complete saturation. The results are given in Table 3. Ligand **B** saturates rapidly, whereas **A** is still increasing after 24 h. To determine the saturation capacities, ligands were therefore left in contact with the metal-ion solutions for 72 h.

On reaction with solutions of transition metals, the ligands appear to undergo some further loss of carbon and nitrogen, presumably by leaching of oligomeric material. There is some consistency, in that losses are higher in solutions of nickel(II) and cobalt(II) than for copper(II) or manganese(II), which may reflect either greater solubility of the oligomer complexes with these metals or the effect of the slightly higher pH in these solutions. The effect is particularly marked for ligand **D**, and substantial for **C**, which were made with the lowest proportions of $Si(OEt)_4$, and are likely to be least cross-linked. It has also subsequently been found [8] that some degradation of the polymers occurs during storage, presumably due to hydrolysis of the Si–O–Si links catalysed by the amine groups. This can be avoided by prior treatment with an acid.

It might be expected that the maximum metal-loading achievable would correspond to one metal ion per diaminoethane group, but it is evident that this stoichiometry is not achieved. In many cases, the composition approximates to (at least) two molecules of diaminoethane per metal ion; this might indicate that 2:1 complexes are formed or that 1:1 complexes are formed and only some of the amine groups are accessible. Provided that it is stereochemically feasible, the formation of 2:1 complexes would probably be favoured on thermodynamic grounds. Further information on the mode of binding was obtained from spectroscopic studies.

TABLE 5. EPR data for copper(II) (^{63}Cu) complexes

Ligand	$g_\perp$	$g_\parallel$	A (mT)
A	2.01	2.22	20
C	2.01	2.23	19.5
D	2.03	2.23	20

EPR spectra were obtained from copper(II) complexes. When the ligands were simply exposed to copper(II) solutions, even for very short periods, the EPR spectra obtained were extremely broad and uninformative. This was presumably due to proximity relaxation, *i.e.* the paramagnetic ions were too close together and rapid spin relaxation occurred. This was overcome by first saturating the ligand with zinc(II) and then exchanging a proportion of the zinc ions by a brief exposure to a copper(II) solution. These materials gave well-resolved EPR spectra showing hyperfine coupling to the copper isotopes (see Table 5). Unfortunately, superhyperfine coupling to the nitrogen atoms of the ligands was not resolved, but the mode of co-ordination of the copper ions can be estimated from the known relationship between g and A values [10]. The observed parameters are similar to those found for discrete $[Cu(en)_2]^{2+}$ complexes. Under the conditions of preparation, it is likely that the copper ions will occupy sites at or very close to the external surface of the solid particles, where it is feasible for each metal ion to have access to two ligand groups.

The electronic reflectance spectra of the copper(II) complexes all gave d–d absorption peaks beyond the range of our spectrometer (> 900 nm). However, spectra were obtained from the nickel(II) complexes, all of which gave one principal absorption at $(15.6\text{–}16.3) \times 10^3$ cm^{-1}. These are presumably ν_2 $[^3A_{2g} \rightarrow {}^3T_{1g}(F)]$ of six-co-ordinate complexes. ν_1 $[^3A_{2g} \rightarrow {}^3T_{2g}]$ was out of range of the spectrometer available. Except for the complex of ligand **B**, ν_3 $[^3A_{2g} \rightarrow {}^3T_{1g}(P)]$ was obscured by strong absorption by the ligands at about 30×10^3 cm^{-1}; for ligand B–Ni^{II}, ν_3 appeared at 27.5×10^3 cm^{-1}. These absorption maxima lie between those for $[Ni(H_2O)_6]^{2+}$ and $[Ni(en)_3]^{2+}$ [11]. The peaks are rather broad, which may indicate that a mixture of species is present, presumably $[Ni(L\text{–}en)(H_2O)_4]^{2+}$ and $[Ni(L\text{–}en)_2(H_2O)_2]^{2+}$ (where L–en represents the bound diaminoethane ligand). The shapes of the absorption peaks suggest that the complexes derived from **A** and **C** contain mostly the 1:1 complex, while **B** and **E** may contain roughly equal amounts of both complexes. This difference from copper reflects the different method of preparation, since here the ligand has been saturated with the metal ion. Under these conditions, formation of 1:1 complexes is more likely.

However, all the data suggest that an appreciable fraction of ligand groups does not carry metal ions. These sites are presumably in the interior of pores which become blocked by the first-bound metal ions. In other cases we have found that the capacity of a given ligand is greater for copper(II) than for nickel(II) or cobalt(II) [4,8,12], and we attribute this behaviour to the different stereochemistry and, hence, different effective bulk of the metal ions and the complexes formed.

Attempts were made to obtain complexes of iron(II), but the green products changed rapidly to brown on exposure to air. Mössbauer spectroscopy showed that these materials contained iron(III) and that from **D** was identical to the product obtained directly from **D** and iron(III) chloride. [IS(Fe)/mm s^{-1}, QS/mm s^{-1}: from **C**, 0.36, 0.84: from **D**, 0.36, 0.77; from **D** and iron(III), 0.37, 0.72].

A preliminary ion-exchange experiment was performed with ligand **D**. A solution with pH 5.5, containing a mixture of nickel(II) and copper(II), was percolated slowly into a column of the ligand. Two bands were formed, with the copper at the top (upstream) indicating, as would be expected, stronger retention of copper(II) than nickel(II). Elution with pH 5.5 buffer solution produced a clear separation between the two bands, while at pH 4.4 the nickel was eluted leaving the copper on the column. The use of related materials in column separation of metal ions will be described more fully later [12].

Acknowledgement

We are grateful to the British Council for travel grants without which this work would have been impossible.

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 I. S. Khatib and R. V. Parish, *J. Organomet. Chem., 369* (1989) 9.
5 R. V. Parish, D. Habibi and V. Mohammadi, *J. Organomet. Chem., 369* (1989) 17.
6 I. S. Khatib, PhD Thesis, University of Manchester, 1985.
7 F. O. Stark, J. Falender and A. P. Wright, in G. Wilkinson, F. G. A. Stone and E. W. Abel (eds.), *Comprehensive Organometallic Chemistry*, Pergamon, New York, 1982, Vol 2, p. 305.
8 I. Ahmed and R. V. Parish, *J. Organomet. Chem., 452* (1993) 23.
9 D. W. Scaufer and K. D. Keefer, in C. J. Clark and D. A. Ulrich (eds.), *Better Ceramics Through Chemistry*, North Holland, New York, 1984.
10 R. V. Parish, *NMR, NQR, EPR and Mössbauer Spectroscopy in Inorganic Chemistry*, Ellis Horwood, Chichester, 1990, p. 190.
11 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 4th edition, Wiley, New York, 1980, p. 787.
12 A. A. El-Nasser and R. V. Parish, *J. Chem. Soc., Dalton Trans.*, submitted.