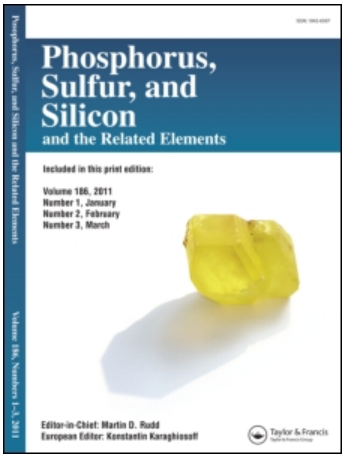

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Publication details, including instructions for authors and subscription information:
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SYNTHESIS AND SOLID-STATE NMR STRUCTURAL CHARACTERIZATION OF POLYSILOXANE-IMMOBILIZED THIOL-AMINE METAL(II) COMPLEXES

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To cite this Article El-nahhal, Issa M.(2000) 'SYNTHESIS AND SOLID-STATE NMR STRUCTURAL CHARACTERIZATION OF POLYSILOXANE-IMMOBILIZED THIOL-AMINE METAL(II) COMPLEXES', Phosphorus, Sulfur, and Silicon and the Related Elements, 162: 1, 245 — 258
To link to this Article: DOI: 10.1080/10426500008045224
URL: http://dx.doi.org/10.1080/10426500008045224

Phosphorus, Sulfur and Silicon, 2000, Vol. 162, pp. 245-258
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SYNTHESIS AND SOLID-STATE NMR STRUCTURAL CHARACTERIZATION OF POLYSILOXANE-IMMOBILIZED THIOL-AMINE METAL(II) COMPLEXES

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(Received February 19, 1999; In final form December 31, 1999)

The polysiloxane-immobilized thiol, amine, and thiol-amine ligand systems P-$(CH_2)_3X$ (where P represents the siloxane network, X=SH,NH_2, or hybride of amine and thiol ligand groups) have been made via the sol-gel process by hydrolytic condensation of $Si(OEt)_4$ and $(MeO)_3Si(CH_2)_3X$. The immobilized polysiloxanes thiol-acetate P-$(CH_2)_3SCH_2COOMe$ and glycinate P-$(CH_2)_3NHCH_2COOMe$ have been prepared by the reaction of the corresponding polysiloxane system P-$(CH_2)_3SH$, or P-$(CH_2)_3NH_2$ with methylchloroacetate. The immobilized thiol-amine ligands form metal(II) complexes when treated with aqueous metal(II) ion solutions (M=Ni^{2+}, Cu^{2+}, Cd^{2+}, Hg^{2+}). High-resolution solid state NMR studies have been used to characterize these immobilized ligand systems and their metal(II) treated samples. ^{29}Si CP-NMR spectra suggest that these ligand systems undergo some leaching(1–4%) of small oligomers when treated with aqueous acid and metal ion solutions. ^{15}N CP-NMR results show that substantial proportion of amine groups is coordinated to metal ions.

Keywords: Siloxane; thiols; thiol-amine ligand; sol-gel

1. INTRODUCTION

Much attention has been focussed on the synthesis of polysiloxane-immobilized ligand systems in which one or two different ligand groups are incorporated into the polymer siloxane systems [1–7]. These immobilized ligand systems include thiols [1], amines [1,2,6], phosphines, phosphine-amines, phosphine-thiols [3,4], and thiolamines [5]. There were many other systems in which the functionalised ligand groups are

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anchored onto the surface of silica [8–10]. In the last few years, solid state NMR techniques along with other chemical tools have been used for characterisation of their molecular structural properties [11–20]. The immobilized amine ligand hows high potential for metal uptake from aqueous solutions and form stable metal(II) complexes [2,6]. In this paper the immobilized thiol-amine hybride ligand system is treated with aqueous metal(II) ions to form complexes. Solid state NMR was used to characterize their strutural properties. ^{29}Si CP-MAS NMR is used to provide information about the different silicon attachments and the stability of the siloxane polymer network (e.g. leaching of small oligomers when treated with acid and metal(II) solutions). CP-MAS of ^{13}C, ^{15}N and ^{1}H CRAMPS NMR results are used to provide information on the interaction of ligand groups with the polysiloxane surface or with the metal ion.

2. EXPERIMENTAL AND INSTRUMENTATIONS

2.1 NMR experiments

^{13}C CP-MAS NMR experiments were carried out at 25.1 MHz on a home-built spectrometer using cross polarization (CP) and magic angle spinning (MAS) with high power ^{1}H decoupling [21]. The ^{13}C CP-MAS spectra were obtained with a 1ms CP contact time and a 1s recycle time. ^{15}N CP-MAS experiments were carried out at 20.3 MHz on a modified Nicolet Nt-200 spectrometer, using a 2.5 cm^3 Chemagnetic Pencile MAS system. The optimized parameter for ^{15}N CP-MAS NMR experiments were a 0.6 ms CP contact time and 0.6 s recycle time. ^{29}Si CP-MAS experiments were carried out at 39.7 MHz on the Nt-260 spectrometer. All ^{29}Si CP-MAS shown in this paper were taken with 2ms CP contact time and 1s recycle time. Solid state ^{1}H NMR experiments were carried out at 360 MHz on modified nicolet NT-360 spectrometer by the combind rotation and multiple-pulse spectroscopy (CRAMPS) techniques [22,23].

2.2 Starting Materials

The 3-aminopropyltriethoxysilane, 3-mercaptotrimethoxysilane, tetraethylorthosilicate and methylchloroacetate were purchased from the Aldrich

Chemical Company and used as received. The metal(II) chlorides were obtained from Mallinkckrodt. The various polysiloxane ligand systems were prepared as previously described [1,2,5,7] as fellow:

Preparation of polysiloxane-immobilized amine ligand system

This ligand system was made as previously described [1–2] by mixing $Si(OEt)_4$ and $(MeO)_3Si(CH_2)_3NH_2$ with a molar ratio 2:1 respectively (Analysis, 3.7 mmol Ng^{-1}, reported: 3.0 mmol Ng^{-1}).

Prepartion of polysiloxane-immobilized thiol ligand system

This immobilized ligand system was made using the previously described method [1] using $Si(OEt)_4$ and $(MeO)_3Si(CH_2)_3SH$ in 2:1 molar ratio in methanol using $(n\text{-}Bu)_2Sn(OCOCH_3)_2$ as catalyst (Analysis 3.3 mmol Sg^{-1}, reported: 3.4 mmol Sg^{-1}).

Preparation of polysiloxane-immobilized thiol-amine ligand system

This ligand system was made as previously described [5] by mixing $Si(OEt)_4$ and $(MeO)_3Si(CH_2)_3SH$ and $(EtO)_3Si(CH_2)_3NH_2$ in the appropriate molar ratio in methanol. (Analysis 2.4 mmol Ng^{-1}, 2.5 mmol Sg^{-1}, reported: 2.4 mmol Ng^{-1}, 2.6 mmol Sg^{-1}).

Preparation of Polysiloxane thiol-acetate system

This system was prepared as previously reported [7] by reacting the mercaptopolysiloxane ligand system with methylchloroacetate at 120°C. The product was filtered and dried in vacuo (0.1 torr) at 100 °C.

Preparation of Polysiloxane glycinate ligand system

This polysiloxane-immobilized ligand system was prepared as previously made [7] by refluxing the polysiloxane monoamine system with methylchloroacetate at 120 °C under nitrogen. The product was then filtered, washed and dried in vacuo (0.1 torr) at 80°C.

2.3 Preparation of metal(II) complexes of the immobilized thiol-amine ligand systems

The metal(II) treated samples are prepared when 0.5 g portion of the immobilized ligand system was shaken with an excess (50 cm^3) of the

desired aqueous metal(II) ion solution(0.1 mol dm^{-3}) for 24 hours. The reagents used were nickel(II) chloride, copper(II) chloride, and cadmium(II) chloride and mercury(II) chloride. The metal(II) treated samples were filtered washed with successive 30 cm^3 portions of water, methanol and diethyl ether and dried at 100°C in vacuum for 24 hours. The resulting solids were analyzed for metal and nitrogen contents by elemental analysis. The results are given in Table I.

TABLE I Microanalysis of thiol-amine polysiloxane and its metal(II) complexes

Complexes	*%N*	*%S*	*%M*	*N/M*[a]	*% Ligand loss*[b]
Thiol-amine	3.6	7.9			
Ni(II) complex	2.9		2.5	4.7	1.8
Cu(II) complex	3.1		1.6	8.6	2.3
Cd(II) complex	3.4		2.6	10.4	4.1
Hg(II) complex	3.2		4.8	9.6	2.4

a. Molar ratio found of nitrogen to metal calculated from elemental analysis.
b. Leaching % of ligand when treated with aqueous metal solution.

3. RESULTS AND DISCUSSION

3.1 Preparations

The three polysiloxane-immobilized ligand systems, thiol-acetate, amine-acetate and thiol-amine were made as previously described [5,7]. In the case of the thiolacetate and amine-acetate ligand systems, solid-state ^1H NMR approach was used to characterized their structures. These two ligand systems and its treatment with divalent metal ions have been described recently [24]. The thiol-monoamine ligand system was treated with aqueous solutions of divalent metal ions (Ni^{2+}, Cu^{2+}, Cd^{2+}, Hg^{2+}) forming metal(II) chelate complexes. Complexation to metal ions was confirmed by ^{13}C and ^{15}N NMR spectra. In these complexes the metal ion is probably coordinates to amine or thiol centers. The elemental analysis of the thiol-amine ligand system and its metal(II) chelate complexes are given in Table I. The fact that the N/M ratio falls between 5 and 10 could simply mean that some amine groups are not accessible. This was con-

firmed by ^{15}N NMR spectra later. There is no evidence that the thiol groups are coordinated to the metal ions. The presence of thiol groups mixed with amine ligand groups in the thiol-amine polysiloxane system has reduced the leaching percentage to (2–4) compared with the case where there are only amine groups present.

NMR Spectra

3.2 ^{13}C CP-MAS NMR results

The ^{13}C CP-MAS NMR spectra of polysiloxane-immobilized thiol-monoamine ligand system and its treatment with HCl have been previously described [5]. The ^{13}C CP-MAS NMR spectra of this ligand and its products of treatment with acid and aqueous divalent metal ion solutions (M=Cu^{2+}, Cd^{2+}, Hg^{2+}) are shown in Fig. 1. The ^{13}C CP-MAS NMR chemical shifts are summarized in Table II. These assignments are based on ^{13}C CP-MAS NMR spectra obtained from literature [5,6,13–20]. The ^{13}C CP-MAS NMR spectrum for the immobilized thiol-monoamine ligand shows three signals at 11.9, 28.0 and 44.7 ppm. These were assigned due to C1,C2 and C3 respectively as reported before [5] (Fig. 1a and Table II). The middle signal splits into a doublet (28.3 and 22.3 ppm) on protonation with HCl 0.11 M (Fig. 1b). This signal is attributed to middle carbon C2. The substantial increasing in shielding of C2 upon protonation was supported by previous reported studies (5,13,16). The ^{13}C NMR spectra of the metal(II) treated samples Figs. 1c – 1e show similar pattern to that of the protonated immobilized ligand systems in which the middle signal has a slight broadening in the spectra of the Cd(II) and Hg(II) complexed thiol-amine. This implies that not all ligand amine sites are accessible to metal ions, therefore the uncoordinated sites may have somewhat different chemical shifts. The unclear picture is probably due to the presence of different complexation forms of ligand groups with metal ions, e.g. the number of ligands complexed with each metal. The broad signal observed in ^{15}N NMR spectrum of Cd(II)-treated sample may also suggest that a portion of ligand groups are not involve in coordination and remain uncoordinated to Cd^{2+} ions.

Dipolar-dephasing experiments for three dipolar-dephasing periods 2.0, 20 and 50 μs were conducted. In a dipolar-dephasing experiment after the CP step, the ^{1}H decoupling power is turned off for a period of time with pulse in the middle, before initiation of acquisition of ^{13}C signals under of

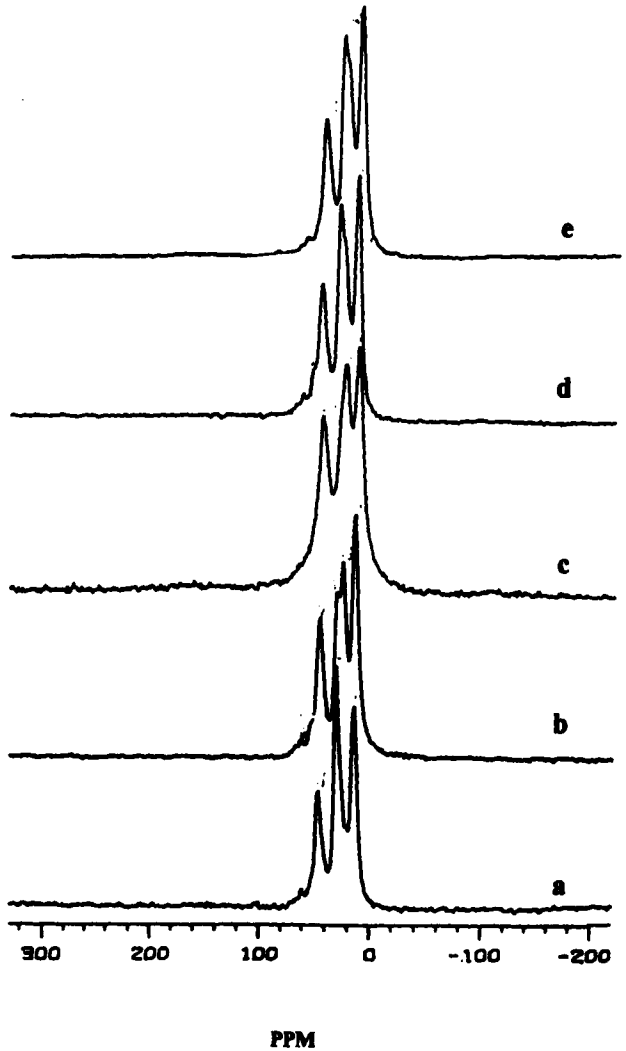


FIGURE 1 ^{13}C CP-MAS NMR spectra of polysiloxane-immobilized thiol-monoamine ligand and its metal treated samples. (a) untreated; (b) protonated; (c) Cd^{2+}-treated; (d) Hg^{2+}-treated; (e) Cu^{2+}-treated

^{1}H high-power decoupling. The dipolar-dephasing spectra of polysiloxane-immobilized thiol-monoamine system and its Cd(II) complex are shown in Figs. 2 and 3 respectively. The dephasing rate of the ^{13}C magnet-

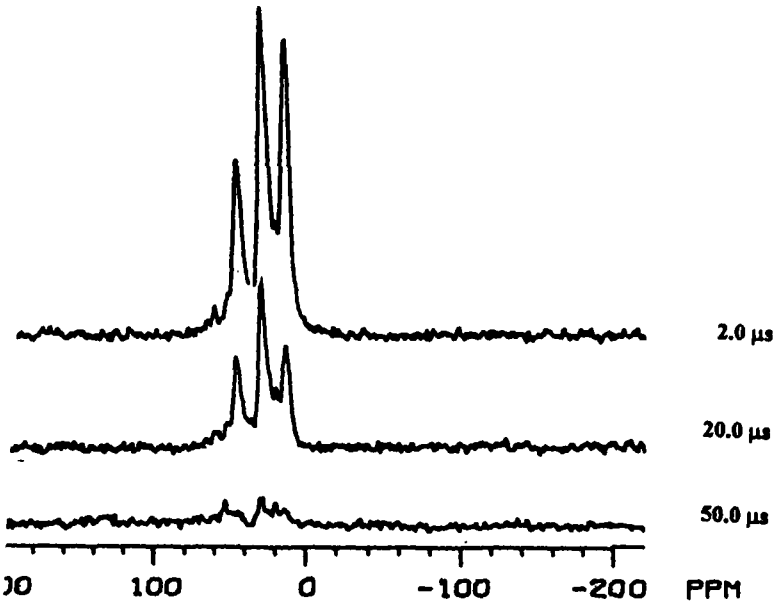


FIGURE 2 Dipolar-dephasing ^{13}C CP-MAS NMR spectra of the untreated polysiloxane-immobilized thiol-monoamine ligand system

ization of the uncomplexed polysiloxane-immobilized thiol-monoamine system (Fig. 2) decreases in the order C1 > C2 > C3 (C3 attached to amine group). In the ^{13}C dipolar dephasing spectra of Cd(II) complex of the immobilized thiol-monoamine (Fig. 3) all carbon atoms dephased slightly more than that of the free immobilized thiol-monoamine ligand system (Fig. 2). From these observations and from the ^{15}N NMR results (Fig. 5), it appears that substantial proportion of the amine ligand groups is involved in complexation with Cd^{2+} ions. This was similar with those reported for amine ligands complexes [6].

3.3 ^{29}Si CP-MAS NMR spectra

The ^{29}Si CP-MAS NMR spectra are expected to provide useful information on the nature of attachments of various types of silicon atoms and on the stability of the attachments of these ligand systems upon treatment with aqueous metal ion solutions. The spectral assignments are based on

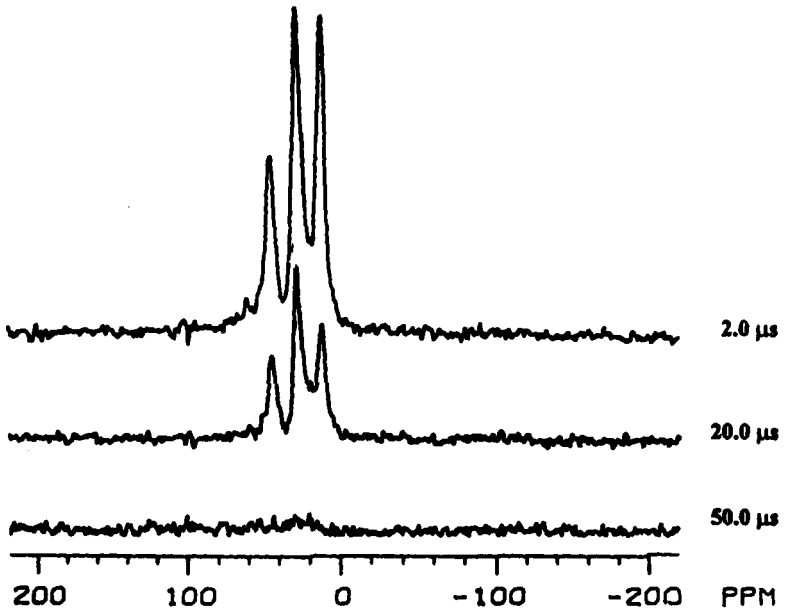


FIGURE 3 Dipolar dephasing ^{13}C CP-MAS NMR spectra of the Cd^{2+} treated of polysiloxane-immobilized thiol-monoamine

solid-state ^{29}Si NMR data taken from literature [13–20]. The ^{29}Si NMR spectra for polysiloxane-immobilzed thiol-amine ligand system and its metal(II) complexes are shown in Fig. 4. The spectra exhibit two major regions of intensities centered at −105 and- 60 ppm relative $Si(O)_4$ and $YSi(O)_3$ units respectively, where Y=-$(CH_2)_3SH$, (-$CH_2)_3NH_2$. The spectra region at −105 ppm is composed of three peaks or shoulders at −109, −100 and −92 (sh) ppm correspond to $(\equiv SiO)_4Si$, $(\equiv SiO)_3SiOH$ and $(\equiv SiO)_2Si(OH)_2$ sites (Fig. 4). The spectral region centered at −60 ppm is composed of a peak at −64 ppm and a shoulder at −57 ppm which assigned due to $(\equiv SiO,)_3SiY$, $(SiO)_2SiYOR$ species respectively where (R=H, CH_3, C_2H_5).

Fig. 4b shows the ^{29}Si CP NMR spectrum of polysiloxane-immobilized thiol-monoamine after treated with 0.11M aqueous HCl solution, the spectrum of the sample treatment with aqueous HCl Fig. 4b has higher relative intensity in the −105 region in comparison to the −60 ppm region compared with the spectrum of untreated sample (Fig. 4a). The spectrum

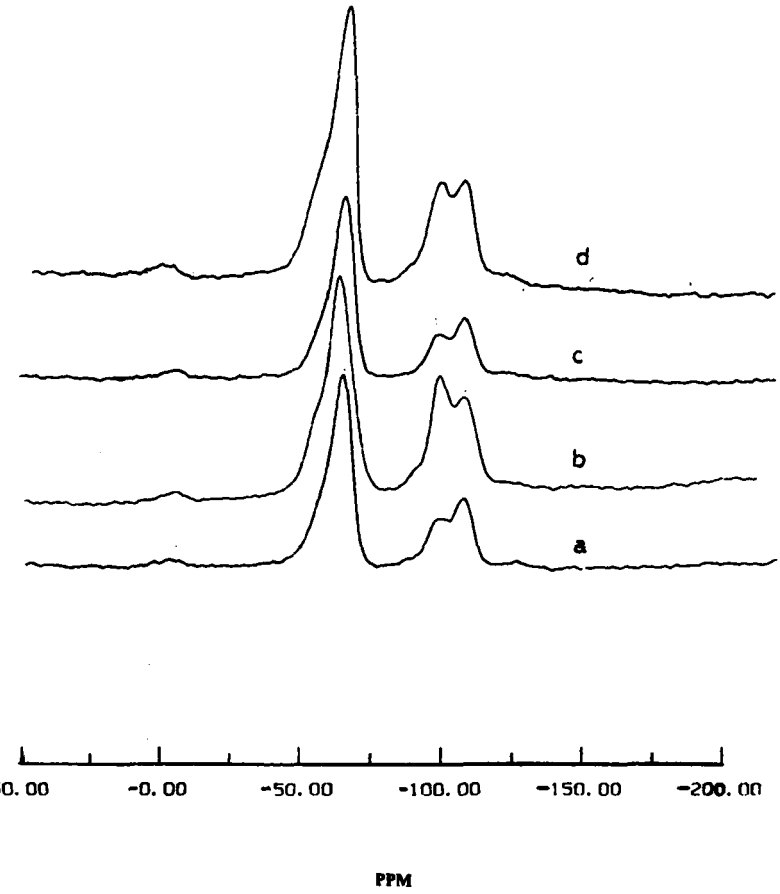
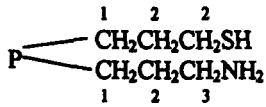


FIGURE 4 ^{29}Si CP-MAS NMR spectra of polysiloxane thiol-monoamine ligand system, (a) untreated; (b) HCl-treated; (c) Cd^{2+}-treated; (d) Hg^{2+}-treated.

shows increase in relative intensities of peaks at −57,-90, and −100 ppm. The reason for these changes is probably correspond to hydrolysis of some Si-O-Si linkages upon treatment with acid solution. Fig. 4d shows the ^{29}Si NMR spectrum of polysiloxane-immobilised thiol-monoamine after treatment with 0.1M Cd(II) aqueous solution, the changes upon treatment with Cd(II) solution are similar to those observed when the immobilized ligand is treated with aqueous acid. This may confirm that there is some leaching of small oligomers from the bulk upon treatment with acid. This was supported by the gravemetric analysis given in Table I.

TABLE II ^{13}C NMR Chemical shifts of polysiloxane-immobilized thiol-monoamine and its metal ion treated samples



Sample	Chemical Shifts/ppm			
	C_1	C_2		C_3
Thiol-amine ligand	11.9	–	28.0	44.7
Thiol-amine - H^+	12.0	22.8	28.3	43.7
Cadmium – sample	11.9	23.1	27.4	43.3
Mercury – sample	12.2	24.2	28.2	44.6

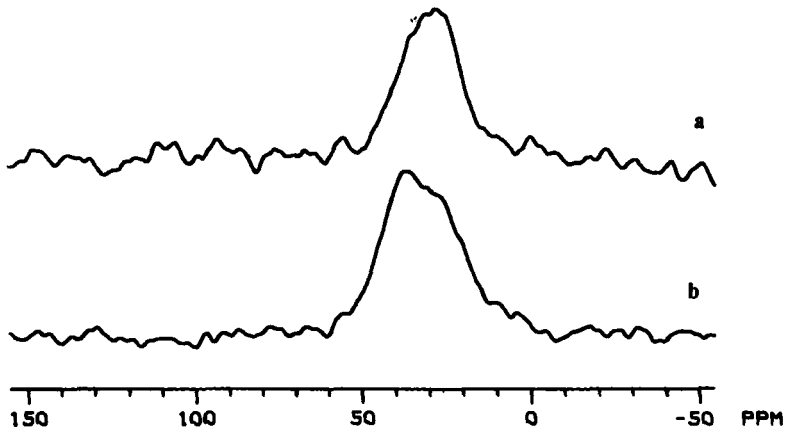


FIGURE 5 ^{15}N CP-NAS NMR spectra of polysiloxane thiol-monoamine and its cadmium complex. (A) untreated; (B) Cd^{2+}-treated

3.4 ^{15}N CP-MAS NMR Spectra

Despite the low natural abundance of the nitrogen (0.37%), and without employing the ^{15}N-enriched samples, valuable information about the sta-

tus of the amine groups and their involvement on coordination with metal ion treated samples are obtained. The ^{15}N NMR spectra of the polysiloxane-immobilized thiol-monoamine and the treated metal(II) compounds are shown in Fig. 5a-b. The spectral assignments are based on solid state ^{15}N NMR data of analogous polysiloxane amine ligands [5]. In these immobilized ligands, the amine form $-NH_2$ and the free ammonium cation $-NH_3^+$ of the immobilized amine ligands occur at 25 and 45 ppm respectively. The ^{15}N NMR spectra of the Cd(II) complex derived the immobilized thiol-amine ligand Fig. 5b show a broad signal of maximum intensity around 40 ppm and a shoulder around 30 ppm. This appears at lower shielding than for the corresponding uncomplexed ligand system (Fig. 5a) which has maximum at 28 ppm. This may suggest that substantial proportion of amine groups is involved in coordinated to the metal ion.

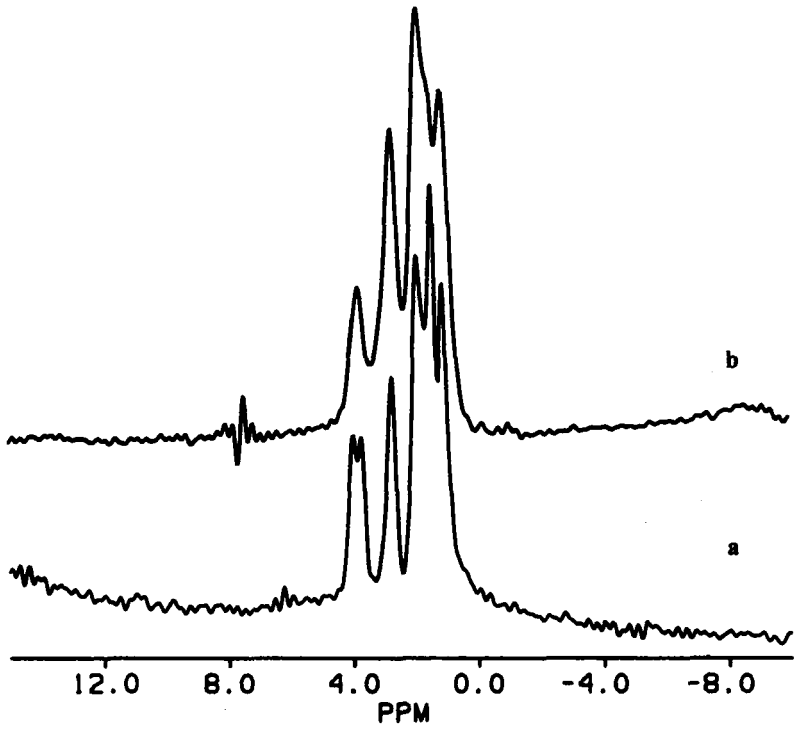


FIGURE 6 ^1H CRAMPS NMR spectra of (a) Polysiloxane thiol ligand system; (b) Polysiloxaned-thiol-acetate ligand

TABLE III ^{1}H NMR chemical shifts of polysiloxane-immobilized thiol, thiol-acetate, amine and amine-acetate ligand systems

$$\overset{1}{P}\text{-}\overset{2}{CH_2}\overset{3}{CH_2}\overset{H}{CH_2}NR \quad ; \quad R = H, R = \overset{3}{CH2}\,COOMe$$

$$\overset{1}{P}\text{-}\overset{2}{CH_2}\overset{3}{CH_2}CH_2SR \quad ; \quad R = H, R = \overset{3}{CH_2}\,COOMe$$

Compound	*Chemical shifts/ppm*				
	H_1	H_2	H_3	NH_2	*Others*[a]
Amine ligand	0.80	1.72	2.73	–	1.23
Amine-acetate ligand	0.96	1.88	3.03	7.88	
Thiol-ligand	1.10	1.85	2.72		1.44 3.72, 3.96
Thiol-acetate ligand	1.04	1.80	2.65		1.48 sh, 3.70

a. These signals are associated with unhydrolyzed -OMe and -OEt groups.

3.5 ^{1}H CRAMPS results

The ^{1}H NMR spectra of polysiloxane-immobilized thiol and thiol-acetate, monoamine, and glycinate ligand systems are shown in Figs. 6 and 7. The chemical shifts assignments given in Table III are based on ^{1}H NMR results obtained from literature [5–6]. The ^{1}H NMR spectra of polysiloxane-immobilized thiol (-SH) Fig. 6a and thiol-acetate ligand Fig. 6b P-$(CH_2)_3SCH_2COOMe$ show sharp line spectra compared with that of polysiloxane-immobilized monoamine and glycinate ligand systems Fig. 7. The line width may suggest the possibility of hydrogen bonding between ligand.

4. CONCLUSION

The polysiloxane-immobilized thiol-amine ligand systems react with aqueous solutions of divalent metal ions forming metal(II) chelate complexes. The ^{29}Si NMR results suggest that these immobilized ligand systems and analogous to the immobilized amine ligand systems are undergo some leaching of small oligomers upon treatment with aqueous solutions

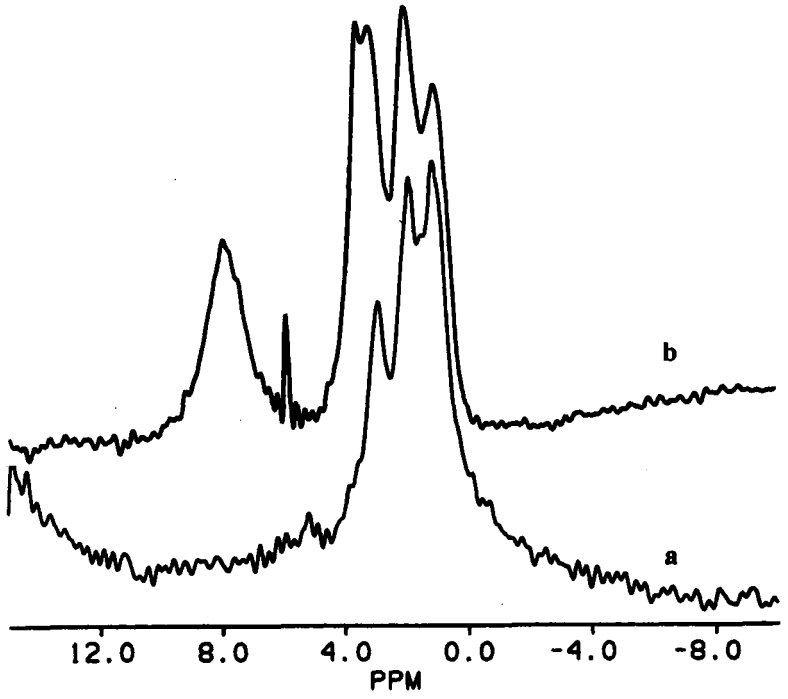


FIGURE 7 ^{1}H CRAMPS NMR spectra of (a) Plysiloxane monoamine ligand; (b) Polysiloxane methyl glycinate ligand

of metal ions or acids. ^{15}N NMR spectra results show that substantial proportion of the amine groups are coordinated to the metal ions.

Acknowledgements

This work was done in the NMR center at Colorado State University. The author wishes to thank Prof. Gary E. Maciel and his group for their great help in obtaining the NMR results. The author also is especially grateful for a Fulbright fellowship.

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