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Synthesis of new dithiocarbamate-based organosilanes for grafting on silica

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Abstract—A new and mild method was developed for the chemoselective conversion of mono-, bis- and tris-aminosiloxanes into their corresponding mono-, bis- and tris-dithiocarbamates, using alkaline hydrides and carbon disulfide in THF. Enhanced scavenging capacity towards mercury ions was observed when these compounds were grafted on silica compared to amine-functionalized silicas or to commercial resins bearing dithiocarbamate moieties.

Dithiocarbamates are bifunctional ligands which have received a great deal of attention due to their wide use as agrochemicals,[1] pharmaceuticals,[2] intermediates in organic synthesis,[3] as protecting group in peptide synthesis[4] or as chelators in material chemistry.[5]

A few efficient and safe methods for the synthesis of dithiocarbamate derivatives with different substitution patterns at the thiol chain have recently been reported in the literature.[6] However, the simple addition of an amine to carbon disulfide to form dithiocarbamate salts is generally conducted under harsh conditions (use of strong basic conditions, high reaction temperatures and long reaction times) to isolate the desired compounds in good yields.[7] Alternative mild methods have been developed but require toxic reagents such as bis(tributyltin)oxide.[8,1c,2c] It is also noteworthy that most of these reactions are generally conducted with secondary amines, which are more nucleophilic than primary ones. In our research programme towards dithiocarbamate modified aminosilanes for the preparation of polymeric materials possessing specific physico-chemical properties, a simple and high-yielding preparative procedure was required to convert aminotrialkoxysilanes into their corresponding dithiocarbamates. Strong and nucleophilic bases like sodium or potassium hydroxide, which are generally used to promote the formation of dithiocarbamate salts from amines and carbon disulfide,[7] are incompatible with the siloxane moiety and yield hydrolysis and/or degradation products. Transformation of aminosiloxanes into dithiocarbamates has only been reported one time in the literature using alkoxides or triethylamine as base.[9] However, in our hands, these methods suffered from several drawbacks as incomplete conversion of the starting aminosiloxane using Et_3N, even after extended reaction times, or undesired attack of the alkoxide on the trialkoxysilane moiety. In this Letter, we report the rapid and clean conversion of mono-, bis- and tris-aminosiloxanes into their corresponding mono-, bis- and tris-dithiocarbamates using alkaline hydrides in THF. We also show that scavenging activity of silica surfaces modified with compound **4a** is excellent.

To understand the underlying mechanisms and to improve reaction yields, we have investigated several reaction parameters to convert 3-aminopropyltrimethoxysilane **1** into its dithiocarbamate derivative **2** (Scheme 1) and we have found that the reaction was sensitive to the amount of carbon disulfide, base and solvent.

Among the inorganic and organic bases tested here (i.e., NaH, K_3PO_4, MeONa, EtONa, *t*-BuONa and Et_3N), NaH and *t*-BuONa were the most effective ones.

Keywords: Nucleophilic addition; Aminotrialkoxysilanes; Dithiocarbamates; Polyanions; Chelates.

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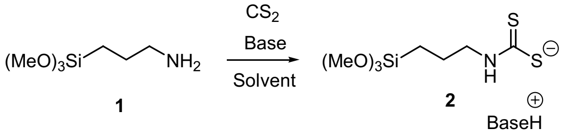


Scheme 1.

Incomplete conversion was observed with K_3PO_4, MeONa, EtONa and Et_3N giving 25%, 80%, 92% and 61% of product, respectively, even after extended reaction times. Moreover, alkoxy group exchange was observed (up to 25%) when EtONa was used for the transformation of **1**. This side reaction was not observed using the sterically hindered *t*-BuONa alkoxide. We have then further optimized the reaction conditions using NaH or *t*-BuONa and we found that good yields of **2** (91–97%) could be attained using a CS_2/**1** molar ratio of 1.5/1. Among the screened solvents, the best results were obtained in THF. Temperature also had an influence on the reaction yield. Complete conversion of **1** can be achieved by adding simultaneously **1** and carbon disulfide to NaH or *t*-BuONa at 0 °C, followed by heating to 65 °C for 2 h. Lowering the reaction temperature to 25 °C resulted in a decrease of the reaction yield to only 47%. Under these optimized conditions, dithiocarbamate **2** was isolated in a quantitative yield. Using *t*-BuONa instead of sodium hydride did not offer any advantage in terms of production yield. Subsequent studies were thus performed with hydrides.

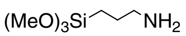
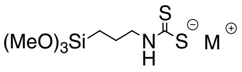
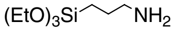
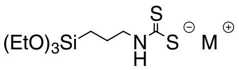
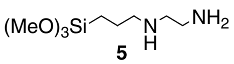
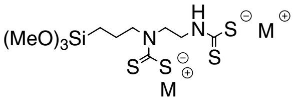
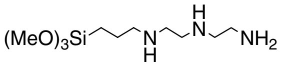
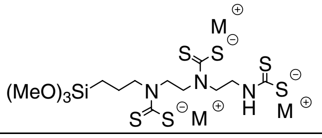
We have then examined the influence of the metal hydride in the same reaction, and it was found that lithium and potassium hydride promoted the addition of 3-aminopropyltrimethoxysilane **1** to carbon disulfide to give the corresponding dithiocarbamates in 99% yield (Table 1, entries a and c).

Under the optimized conditions, a brief study of the scope of the reaction was undertaken with various commercially available mono-, bis- and tris-aminosiloxanes;[10] the results are summarized in Table 1. They demonstrate that the use of alkaline hydrides in THF between 0 and 65 °C is a very simple and convenient method for the synthesis of dithiocarbamate-functionalized aminosiloxanes. Using **1**, **3**, **5** or **7** as starting materials, the conversion was complete at 65 °C within 2 h and products **2**, **4**, **6** and **8** were obtained in excellent yields. It is noteworthy that selective monodithiocarbamation of *N*-[3-(trimethoxysilyl)propyl] ethylenediamine **5** could not be achieved with 1.0 equiv of carbon disulfide. Using sodium hydride as a base, ^1H NMR showed that complex mixtures containing the starting diamine, **6b** and monodithiocarbamation products were obtained. The cyclic urea arising from nucleophilic attack of a nitrogen atom on the intermediate monodithiocarbamate has however never been detected under our experimental conditions when starting from **5**. All the synthesized compounds **2**, **4**, **6** and **8** were obtained as yellow solids and were characterized by ^1H and ^{13}C NMR spectroscopies, FT-IR, and elemental analyses. Dithiocarbamates **2**, **4**, **6** and **8** were soluble in DMSO, alcohols and THF at room temperature and in hot toluene. No carbon disulfide loss or isothiocyanate formation was observed when these compounds were heated in refluxing THF or toluene for 15 h.[11]

To demonstrate the usefulness of such dithiocarbamate-functionalized organosilanes when used to prepare silica-based adsorbents, a silica gel sample was grafted with compound **4a** and the binding properties of the resulting organosilica towards Hg(II) species were evaluated and compared to the corresponding amine-functionalized silica gel as well as to a commercially available resin bearing dithiocarbamate moieties (Sumichelate Q10R).

Two-step syntheses of dithiocarbamate-functionalized silicas have already been described in the literature: (i) grafting of aminosiloxane **1** onto the silica surface,

Table 1. Dithiocarbamation of mono-, bis- and tris-aminosilanes[a]

Entry	Aminosilane	MH	Products	Product (yield, %)[b]
a	 **1**	LiH		**2a**, 99
b		NaH		**2b**, 97
c		KH		**2c**, 99
d	 **3**	LiH		**4a**, 98
e		NaH		**4b**, 95
f		KH		**4c**, 98
g	 **5**	LiH		**6a**, 99
h		NaH		**6b**, 96
i		KH		**6c**, 95
j	 **7**	LiH		**8a**, 98
k		NaH		**8b**, 98
l		KH		**8c**, 96

[a] The reactions of **1** or **3** (10 mmol) with CS_2 in the presence of MH (12 mmol) were carried out in THF (20 mL) between 0 and 65 °C. Dithiocarbamation of **5** (10 mmol) was performed with MH (24 mmol) and CS_2 (30 mmol). Dithiocarbamation of **7** (10 mmol) was performed with MH (36 mmol) and CS_2 (45 mmol).

[b] Isolated yields.

(ii) reaction of the aminopropyl-grafted solid with carbon disulfide.[12] It is worth noting that the nucleophilic addition of the amine groups on CS_2 was incomplete when made in the absence of alkaline catalyst,[12e] the use of this latter (though applied[12a,b,d]) being not recommended because of the poor chemical stability of the silica network in alkaline medium.[13] Incomplete reaction with carbon disulfide was also reported for aminated resins.[14] Here, grafting silica gel with compound **4a** was successful, providing a dithiocarbamate-functionalized material in one step, free of remaining amine groups, as demonstrated by IR spectroscopy and solid-state ^{13}C NMR experiments. Figure 1 shows the extraction capabilities of the silica gel-immobilized-dithiocarbamate derivative for Hg(II), measured as a function of time from a 0.1 mM $Hg(NO_3)_2$ solution at pH 5 to which the adsorbent was added at 80 or 160 mg L^{-1} (see curves 'a' and 'b'). The data indicate that the rate of the extraction process and the uptake yield are very similar to those attained with the dithiocarbamate-functionalized Sumichelate Q10R resin (see curves 'c' and 'd'). This points out thereby to the effectiveness of the organosilica sorbent. This latter was even more efficient than the resin (compare curves 'b' and 'd'), leading to a slightly higher metal ion capacity (0.70 mmol g^{-1} for organosilica and 0.65 mmol g^{-1} for the resin) in spite of its lower content in chelating groups (1.15 mmol g^{-1} for organosilica and 1.25 mmol g^{-1} for the resin). The utility of the dithiocarbamate-functionalized organosilane precursor was further confirmed by the very low extraction capacity of the aminopropyl-grafted silica sample (see curve 'e'), despite being present in a larger amount in the medium (390 mg L^{-1}), illustrating the enhanced chelating properties of the immobilized ligand in the form of dithiocarbamate. This new class of materials thus looks promising not only for remediation purposes but also for other kind of applications requiring selective recognition properties (as, e.g., Hg(II) sensing subsequent to preconcentration at modified electrodes[15]).

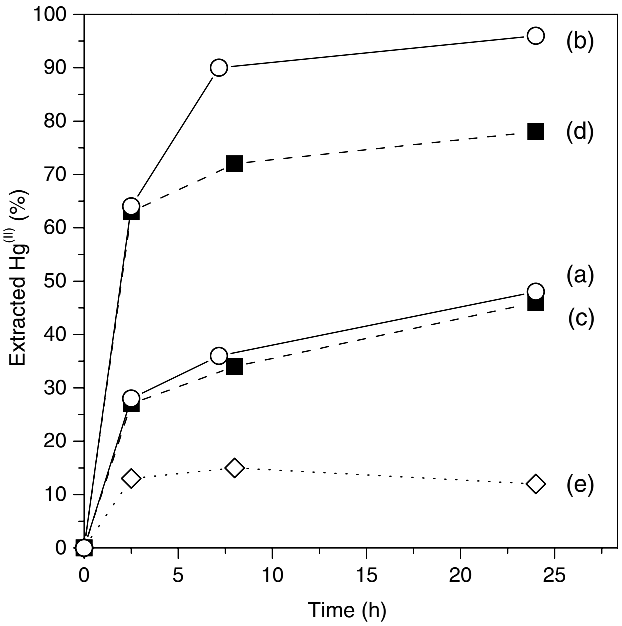


Figure 1. Extraction of Hg(II) as a function of time for dithiocarbamate-grafted silica gel (a, b), Sumichelate Q10R (c, d), or aminopropyl-grafted silica gel (e). Experiments were made from 200 mL of solution containing 1×10^{-4} M $Hg(NO_3)_2$ at pH 5 to which selected amounts of the powdered adsorbents were added: 16 mg (a, c); 32 mg (b, d); 78 mg (e).

In conclusion, we have developed in this study a new procedure for the efficient synthesis of dithiocarbamate derivatives from aminosiloxanes, carbon disulfide and alkaline hydrides in THF. The synthetic procedure is generally applicable to a wide range of aminosiloxanes and allows the preparation of mono-, bis- and tris-dithiocarbamates in excellent yields. Silica grafted with compound **4a** shows enhanced binding properties towards Hg(II) species compared to amine-modified silica or commercial resin bearing dithiocarbamate moieties. The present protocol should thus facilitate the further exploitation of this unique class of dithiocarbamate-based silanes for the preparation of new types of scavenging materials, and should open the way of getting highly efficient mercury adsorbents based on dithiocarbamate-functionalized mesoporous silicas prepared in one step by the sol–gel process, as reported for other organic–inorganic hybrid materials.[16]

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10. All compounds gave satisfactory analytical data. Described below are representative procedures and spectral data for compounds **4b**, **6b** and **8b**.

    Synthesis of compound **4b**. To a suspension of degreased sodium hydride (12 mmol) in dry THF (20.0 mL) cooled to 0 °C were added dropwise via syringe carbon disulfide (15 mmol) and 3-aminopropyltriethoxysilane **2** (10 mmol). After being stirred at 0 °C for 0.5 h, the reaction mixture was refluxed for 2 h under vigorous stirring. After cooling, the volatiles were removed under reduced pressure. The crude solid obtained was purified by washing with dry Et_2O to afford **4b** in 95% yield. ^1H NMR (400 MHz, DMSO-d_6): $\delta = 8.04$ (br t, NH), 3.74 (q, $J = 7.2$ Hz, 6H), 3.33 (td, $J = 5.8$, 5.8 Hz, 2H), 1.64–1.43 (m, 2H), 1.14 (t, $J = 7.2$ Hz, 9H), 0.50 (t, $J = 5.8$ Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): $\delta = 213.9$, 57.7, 49.2, 21.9, 18.1, 7.4. IR (KBr): 3400, 2974, 1631, 1518, 1490, 1294, 1104, 1079, 953 cm^{-1}. Anal. Calcd for $C_{10}H_{22}NNaO_3S_2Si$: C, 37.59; H, 6.94; N, 4.38; Na, 7.20; O, 15.02; S, 20.07; Si, 8.79. Found: C, 37.82; H, 7.04; N, 4.55; S, 20.28.

    Synthesis of compound **6b**. The general procedure described for the preparation of **4b** was used for the addition of *N*-[3-(trimethoxysilyl)propyl] ethylenediamine **5** to carbon disulfide. The reaction was conducted with **5** (10 mmol), CS_2 (30 mmol), sodium hydride (24 mmol) in THF (40.0 mL). ^1H NMR (400 MHz, DMSO-d_6): $\delta = 8.27$ (br t, NH), 4.15 (t, $J = 6.4$ Hz, 2H), 3.94 (t, $J = 6.4$ Hz, 2H), 3.57 (t, $J = 6.4$ Hz, 2H), 3.43 (s, 9H), 2.80–1.52 (m, 2H), 0.48 (t, $J = 8.0$ Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): $\delta = 214.4$, 213.4, 54.8, 50.1, 49.9, 45.1, 19.7, 6.0. IR (KBr): 3338, 2942, 1625, 1492, 1398, 1194, 1090, 959 cm^{-1}. Anal. Calcd for $C_{10}H_{20}N_2Na_2O_3S_4Si$: C, 28.69; H, 4.82; N, 6.69; Na, 10.98; O, 11.47; S, 30.64; Si, 6.71. Found: C, 28.29; H, 5.37; N, 7.02; S, 30.21.

    Synthesis of compound **8b**. The general procedure described for the preparation of **4b** was used for the addition of 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane **7** to carbon disulfide. The reaction was conducted with **7** (10 mmol), CS_2 (45 mmol), sodium hydride (36 mmol) in THF (40.0 mL). ^1H NMR (400 MHz, DMSO-d_6): $\delta = 8.57$ (br t, NH), 4.30 (t, $J = 6.0$ Hz, 2H), 4.25–4.12 (m, 4H), 4.02–3.92 (m, 4H), 3.46 (s,9H), 1.72–1.61 (m, 2H), 0.46 (t, $J = 6.0$ Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): $\delta = 215.4$, 214.7, 213.8, 56.4, 50.8, 49.6, 48.1, 48.0, 46.7, 21.3, 7.1. IR (KBr): 3345, 2974, 2942, 1463, 1397, 1189, 1039, 959 cm^{-1}. Anal. Calcd for $C_{13}H_{24}N_3Na_3O_3S_6Si$: C, 27.89; H, 4.32; N, 7.51; Na, 12.32; O, 8.57; S, 34.37; Si, 5.02. Found: C, 27.58; H, 4.62; N, 7.63; S, 33.95.

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