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N,S Ligands for Preconcentration or Elimination of Heavy Metals. Synthesis and Characterisation of Aminoethanethiols and Aminoethanethiol-modified Silica Gel

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Molecular (N,S) aminothiols $R(CH_2)_3NH(CH_2)_2SH$ (**1**), $R(CH_2)_3NH(CH_2CHMe)SH$ (**2**), $R(CH_2)_3NH(CH_2)_2S(CH_2)_2SH$ (**3**), $R(CH_2)_3NH(CH_2CHMe)S(CH_2CHMe)SH$ (**4**) and $R(CH_2)_3N[(CH_2)_2SH]_2$ (**5**) [$R = (EtO)_3Si$] have been prepared by a one step reaction of olefin sulfide on aminopropyltriethoxysilane and characterised by physicochemical methods; the grafting of **1** on silica is reported.

During the last decade, much of the current interest in the synthesis and metal coordination of multidentate aminothiol (N, S) ligands[1] was related to their application in bioinorganic chemistry (enzyme modelisation) and in medical imaging. More recently, the use of these ligands was extended to environmental problems, first because of their good complexing properties towards heavy metals such as Zn, Cd or Hg which allowed metal depollution and secondly because they can be functionalised by a triethoxysilane group and thus easily grafted on a silica support to give supported molecular traps.[5]

We have, in a long term objective, performed the synthesis of a series of tuneable aminothiol ligands directed to heavy metal speciation, concentration or elimination. Here we describe the synthesis of the ligands resulting from the one-step reaction directed from the reaction of olefin sulfide on aminopropyltriethoxysilane (Scheme 1).

Five compounds were isolated as liquids, after fractional distillation and characterised by spectroscopic data. **1**, **2** and **5** resulted from the monoinsertion (**1**,**2**) and diinsertion (**5**) reaction of the olefin sulfide in the N—H bond while **3** and **4** were obtained by the more unusual double insertion reaction of the olefin sulfide in the N—H + S—H bonds. The yields depend on the reaction stoichiometry and the steric hindrance of the olefin sulfide (R = H, Me). They range from 80% for **2** to 33% for **3**.

Compound **1** was grafted on silica (Silica Gel Merck 60 230–400 Mesh) by triethoxysilane hydrolysis. The ^{13}C CPMAS NMR spectrum of the solid indicated that **1** is not grafted on the silica through all the ethoxy groups since the presence of a free SiOEt group is clearly apparent.[24] No change in the donor atoms of **1** is observed after grafting as indicated by comparing the IR spectra of the solid [ν(NH) 3312 cm^{-1}; ν(SH) 2580 cm^{-1}] and pure compound [ν(NH) 3307 cm^{-1}, ν(SH) 2557 cm^{-1}]. A grafting yield of 0.9 mmol g^{-1} was determined from elemental analysis, which agrees with literature data.[12a,23]

Techniques used: ^{1}H and ^{13}C NMR, MS, ^{13}C CPMAS NMR, elemental analysis

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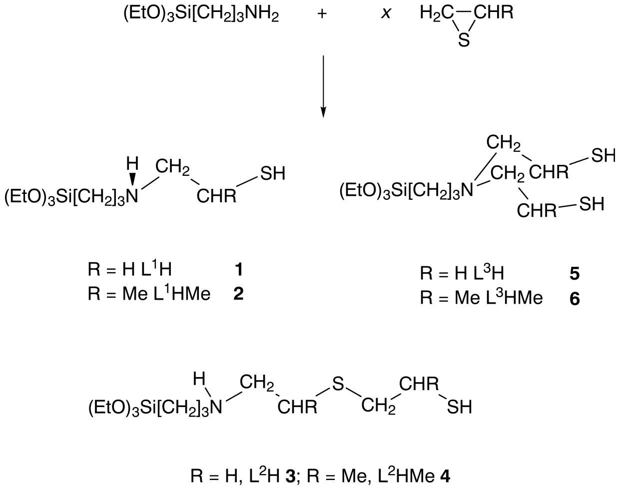

Scheme 1

Tables: 3 (yields for ethylene sulfide and propylene sulfide; ^{13}C NMR)

Figures: 2 (^{13}C-DEPT NMR, Raman spectra)

Schemes: 5

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