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# Formation of extended 1D coordination polymers in tetrathioether complexes of mercury(II): Effect of the organic substituents on the crystal structures of ${Si(CH_2SR)_4}HgBr_2$ (R = Me, Ph)

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#### Abstract

Two novel one-dimensional (1D) coordination polymers of stoichiometry [ $\{Si(CH_2SR)_4\}HgBr_2]_n$  (R = Me, **2a**; R = Ph, **2b**) have been prepared by treatment of HgBr<sub>2</sub> with the functionalized silanes Si(CH<sub>2</sub>SR)<sub>4</sub> (R = Me, **1a**; R = Ph, **1b**) acting as tetradentate thioether ligands. The extended structures result from intermolecular Hg–S interactions linking the monomeric { $Si(CH_2SR)_4$ }HgBr<sub>2</sub> units, as established for **2a**, **b** using single-crystal X-ray diffraction. The effective coordination around the Hg atoms in both compounds is best described as distorted octahedral.

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We have recently reported the synthesis of the bidentate and tridentate thioethers  $R_{4-n}Si(CH_2SR)_n$  (n = 2, 3; R = Me, Ph) and characterized a wide variety of complexes in which they act as either terminal

[1–5] or bridging ligands [6,7]. The latter are particularly interesting since flexible multidentate ligands have the ability to generate diverse coordination networks with potential applications as functional materials [8–10] but the use of polythioethers in such context has received little attention [11–16]. Continuing our studies on multidentate thioethers, we set out to synthesize and evaluate the coordinative properties of the tetrathioether ligands Si(CH<sub>2</sub>SR)<sub>4</sub> (R = Me, **1a**; R = Ph, **1b**). In this regard, Goodall [17]

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investigated almost 40 years ago the coordination chemistry of the related tetrakis[(alkylthio)methyl]methanes  $C(CH_2SR)_4$  (R = Bu<sup>n</sup>, Ph) towards palladium, platinum and mercury. In particular, the Hg(II) ion formed dinuclear complexes [X<sub>2</sub>Hg{C(CH<sub>2</sub>SBu<sup>n</sup>)<sub>4</sub>}HgX<sub>2</sub>] (X = Cl, Br, I) having doubly bidentate chelating ligands, whereas no analogous reaction was observed for the phenyl-substituted thioether ligand. Interested in investigating the effect on structure and reactivity of replacing the central carbon atom in C(CH<sub>2</sub>SR)<sub>4</sub> by silicon, we report herein the synthesis of **1a** (that of **1b** has already been published [18a]) and the reactivity of both ligands towards HgBr<sub>2</sub>.

The tetrathioether Si(CH<sub>2</sub>SMe)<sub>4</sub> (**1a**) was easily synthesized, following a procedure similar to that used to prepare MeSi(CH<sub>2</sub>SMe)<sub>3</sub> [1], by reacting tetrachlorosilane with 4 molar equivalents of LiCH<sub>2</sub>SMe (Scheme 1). Following vacuum distillation (b.p. = 127-130 °C at 0.29 Torr), **1a** was isolated in pure form as a pale yellow liquid in ca. 65% yield.<sup>1</sup>

The complexes  $[{Si(CH_2SR)_4}HgBr_2]$  (R = Me, 2a; R = Ph, 2b) were readily prepared by allowing mercury(II) bromide to react with equimolar amounts of the corresponding thioethers (Scheme 2) and were isolated as white, air-stable solids in 55–80% yield. They are both soluble in chlorinated hydrocarbons and were characterized by a combination of analytical and spectroscopic techniques.<sup>2</sup> Their <sup>1</sup>H NMR spectra (in CDCl<sub>3</sub>) exhibit singlet resonances for the methylene protons ( $\delta$  2.20 and 2.68 ppm for **2a** and **2b**, respectively), both of which are only slightly downfield shifted (ca. 0.15 ppm) relative to the free ligands in the same solvent. More importantly, the presence of only one signal for the four methylene groups in each case (down to 253 K for 2b) is consistent with the presence of highly fluxional (i.e., labile) systems in solution.

SiCl<sub>4</sub> + 4 LiCH<sub>2</sub>SMe 
$$\xrightarrow{\text{pentane}}$$
 Si(CH<sub>2</sub>SMe)<sub>4</sub>  
Scheme 1.

The molecular structures of both 2a and 2b were determined by single-crystal X-ray diffraction.<sup>3</sup> The complexes present in the solid state extended structures in which fairly linear HgBr<sub>2</sub> moieties are connected by doubly bidentate chelating thioether ligands (Figs. 1 and 2). Interestingly, whereas the methyl groups in 2a are arranged in an anti fashion, all the phenyl substituents in **2b** adopt a parallel orientation. The mercury centers in both complexes are in distorted octahedral environments, with the deviation from the ideal geometry being more pronounced in the case of **2b**. In this regard, whereas all the cis S-Hg-S and S-Hg-Br angles in 2a are in the approximate range 84-96°, the corresponding values in 2b span the range 78–99°. Similarly, the deviation from linearity of the Br-Hg-Br angle in 2b [170.70(2)°] is more evident than in 2a [176.73(2)°], a situation that appears to be reflected also in the moderately shorter Hg-Br bond lengths observed in **2b** [2.4521(7) and 2.4540(6) Å] relative to those in 2a [2.5147(5) Å]. The presence of a crystallographically imposed mirror plane which bisects the Br-Hg-Br and C-Si-C angles in 2a leads to the observation of only two unique Hg-S bond lengths [2.955(1) and 3.048(1) A]. In the case of **2b**, although the two *intramo*lecular Hg-S bond distances are very similar [2.989(2) and 2.994(2) Å], the two *intermolecular* interactions are significantly longer [3.201(2) and 3.204(2) Å], a situation which is arguably a consequence of the lower Lewis basicity of the SPh vs. SMe groups. It is also interesting to note that all of these Hg-S bond lengths are considerably longer than the corresponding values (ca. 2.5-2.9 Å) typically observed in a variety of Hg(II) thioether complexes, including polymeric species [19-30].

In conclusion, we have demonstrated that, unlike  $C(CH_2SPh)_4$ , the tetrathioether silane  $Si(CH_2SPh)_4$  coordinates to  $HgBr_2$  and that both **2a** and **2b** display onedimensional extended structures in the crystalline state. However, whereas the intra- and intermolecular Hg-Sinteractions in **2a** are almost identical, the intermolecular Hg-S contacts in **2b** are markedly weaker than the intramolecular ones. Our systematic studies on the coordination chemistry of  $Si(CH_2SR)_4$  (R = Me, Ph) and  $Ge(CH_2SR)_4$  [18b] towards other cadmium and mercury halides will be published elsewhere in the near future.

<sup>&</sup>lt;sup>1</sup> Selected data for **1a**: NMR data (in C<sub>6</sub>D<sub>6</sub>): <sup>1</sup>H  $\delta$  1.88 (s, 12 H, CH<sub>3</sub>), 2.04 (s, 8 H, CH<sub>2</sub>); <sup>13</sup>C  $\delta$  16.4 (t, <sup>1</sup>J<sub>C-H</sub> = 131, 4 C, CH<sub>2</sub>), 20.0 (q, <sup>1</sup>J<sub>C-H</sub> = 138, 4 C, CH<sub>3</sub>). Anal. Calcd. for C<sub>8</sub>H<sub>20</sub>S<sub>4</sub>Si: C, 35.2; H, 7.4; S, 47.0. Found: C, 35.7; H, 7.1; S, 45.7%.

<sup>&</sup>lt;sup>2</sup> Selected data for **2a**: NMR data (in CDCl<sub>3</sub>) <sup>1</sup>H δ 2.20 (s, 8 H, CH<sub>2</sub>), 2.29 (s, 12 H, CH<sub>3</sub>); <sup>13</sup>C δ 16.9 (t, <sup>1</sup>J<sub>C-H</sub> = 133, 4 C, CH<sub>2</sub>), 21.3 (q, <sup>1</sup>J<sub>C-H</sub> = 141, 4 C, CH<sub>3</sub>). Anal. Calcd. for C<sub>8</sub>H<sub>20</sub>Br<sub>2</sub>HgS<sub>4</sub>Si: C, 15.2; H, 3.2. Found: C, 15.2; H, 3.2%. Selected data for **2b**: NMR data (in CDCl<sub>3</sub>) <sup>1</sup>H δ 2.68 (s, 8 H, CH<sub>2</sub>), 7.25–7.37 (m, 20 H, C<sub>6</sub>H<sub>5</sub>). Anal. Calcd. for C<sub>28</sub> H<sub>28</sub>Br<sub>2</sub>HgS<sub>4</sub>Si: C, 38.2; H, 3.2. Found: C, 38.5; H, 3.4%.

<sup>&</sup>lt;sup>3</sup> Crystal data for **2a** (at 100 K): monoclinic, *C2/c*, *a* = 14.4802(11), *b* = 8.9207(6), *c* = 14.1158(10) Å,  $\beta$  = 107.963(1)°, *V* = 1734.5(2) Å<sup>3</sup>, *Z* = 4; structure refined by full-matrix least-squares on *F*<sup>2</sup> to give final indices *R*<sub>1</sub> = 0.0270 and *wR*<sub>2</sub> = 0.0681. Crystal data for **2b** (at 173 K): triclinic, *P*1, *a* = 9.3386(19), *b* = 13.323(3), *c* = 13.879(3) Å,  $\alpha$  = 62.28(3)°,  $\beta$  = 89.62(3)°,  $\gamma$  = 79.84(3)°, *V* = 1499.1(5) Å<sup>3</sup>, *Z* = 2; structure refined by full-matrix least-squares on *F*<sup>2</sup> to give final indices *R*<sub>1</sub> = 0.0364 and *wR*<sub>2</sub> = 0.0774.



Fig. 1. Crystal structure of [ $\{Si(CH_2SMe)_4\}HgBr_2$ ] (**2a**). Selected bond lengths (Å) and angles (°): Hg–S(1) 2.9549(10), Hg–S(2) 3.0481(10), Hg–Br(1) 2.5147(5), and Br(1)–Hg–Br(1)' 176.729(17), Br(1)–Hg–S(1) 92.29(2), Br(1)–Hg–S(1)' 90.12(2), Br(1)–Hg–S(2)'' 89.64(2), Br(1)–Hg–S(2)'' 87.92(2), S(1)–Hg–S(1)' 85.09(4), S(1)'–Hg–S(2)'' 177.96(3), S(1)–Hg–S(2)'' 95.57(3), S(2)''-Hg-S(2)''' 83.84(4).



Fig. 2. View of the crystal structure of [ $\{Si(CH_2SPh)_4\}HgBr_2$ ] (**2b**) along the *x*-axis. Selected bond lengths (Å) and angles (°): Hg–S(1) 2.9888(17), Hg–S(2) 2.9935(15), Hg–S(3) 3.2013(15), Hg–S(4) 3.2037(17), Hg–Br(1) 2.4540(6), Hg–Br(2) 2.4521(7), and Br(1)–Hg–Br(2) 170.695(15), Br(1)–Hg–S(1) 94.77(4), Br(1)–Hg–S(2) 92.33(3), Br(1)–Hg–S(3)' 78.32(4), Br(1)–Hg–S(4)' 94.42(4), Br(2)–Hg–S(1) 92.06(4), Br(2)–Hg–S(2) 94.73(4), Br(2)–Hg–S(3) 94.42(4), Br(2)–Hg–S(4)' 78.55(4), S(1)–Hg–S(2) 83.43(4), S(1)–Hg–S(3)' 98.97(4), S(1)–Hg–S(4)' 170.50(3), S(2)–Hg–S(3)' 170.48(3), S(2)–Hg–S(4)' 98.59(4), S(3)'–Hg–S(4)' 80.57(4).

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### Appendix A. Supplementary data

Crystallographic data for the structural analyses of compounds **2a** and **2b** have been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 260622 and 260623, respectively). Copies of this information may be obtained free of charge from: The director, CCDC, Union Road, Cambridge, CB2 IEZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.inoche.2005.02.008.

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