

The removal of mercury from water by open chain ligands containing multiple sulfurs

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Abstract

Mercury pollution is a serious challenge faced by environmental chemists over the world. For several years now, our group has been developing new compounds to precipitate and thereby remove mercury from water. In this paper, we present a new family of alkyl thiol mercury chelates to add to the aromatic ligands we have previously reported. These new compounds are effective at precipitating mercury from water and with an excess of the best compound, removal is quantitative. Furthermore, the precipitates are stable and released little to no mercury back into solution during leaching studies.

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1. Introduction

Mercury pollution is a global crisis facing society today, and the presence of Hg in groundwater and the oceans will be a problem continuing into the foreseeable future. Due to mercury's use in gold-mining [1–4], chlor-alkali plants [5–6], and chemical synthesis [7,8], as well as its inadvertent release during the combustion of fossil fuels, especially coal [9,10], contamination is now widespread. This is of great concern due to the metal's high toxicity [11–17] and the tendency of organomercurials to bioaccumulate in aquatic foodchains [18]. Therefore, mercury remediation has become a critical global need.

A number of methods have been explored for the remediation of mercury pollution [19]. Phytoremediation, the use of plants to remove contaminants, is one significant area of study and a potentially very cost-effective technique [20–24]. However, many of these methods involve converting organo- or divalent mercury species into metallic mercury, which is then released by the plant as vapor. This has the net effect of simply moving the mercury from water or soil into the atmosphere, where it will eventually precipitate back to contaminate some other site.

Methods that do not result in mercury release require the harvesting of the plants, thereby dramatically increasing the volume of hazardous waste that will require disposal. Filters of various types can be used to remove mercury [25–36]. While many of these are very effective, they all require that the contaminated water be diverted through the filter at a controlled rate. This is very manageable for a wastewater treatment facility, but is not practical for large bodies of water, such as rivers or lakes.

For large bodies of water, the simplest technique is the precipitation of the metal with a ligand. A number of such ligands have been suggested in the past, including sodium *N,N*-dimethyldithiocarbamate (DMDTC) (Fig. 1a) [37], sodium trithiocarbonate (STC) (Fig. 1b) [38], and sodium 1,3,5-triazine-2,4,6-trithiolate (TMT) (Fig. 1c) [39]. All of these ligands are able to precipitate mercury. However, in all three cases there are concerns about the long-term stability of the precipitates, which leach mercury back into the water after the initial precipitation [38]. Furthermore, DMDTC can decompose into thiram, which is toxic to fish and STC decomposes into toxic carbon disulfide, limiting the usefulness of these ligands for *in situ* remediation [38]. TMT is a less effective precipitating agent than the others and the TMT–mercury compound is unstable [39].

A new class of ligands (Fig. 1d and e) [38,40,41] has recently been published by our group which contain aromatic backbones with two terminal thiol alkyl amide arms and binds Hg in a lin-

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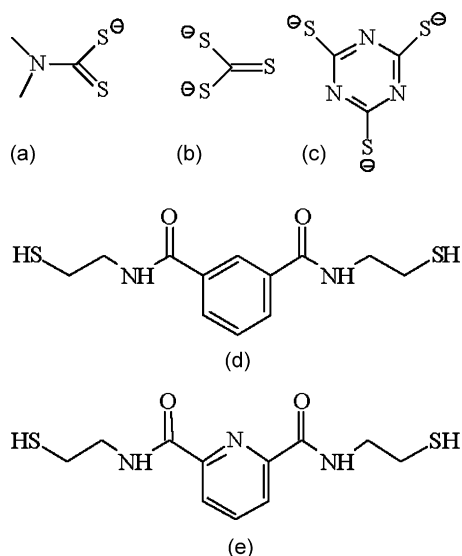


Fig. 1. Mercury precipitation agents: (a) DMDTC, (b) STC, (c) TMT, (d) and (e) recent ligands from the Atwood group.

ear S–Hg–S arrangement [42]. These chelates have proven very effective at removing mercury from water and have been successful in remediating both lab and field samples. The resulting complexes have so far proven very stable to leaching [38,40,41].

This paper describes the synthesis and initial testing of new ligands designed to bind Hg in a tetrahedral geometry. Mercury compounds are known to generally assume either a linear or tetrahedral geometry [43,44] and studies have shown that ligands which cannot permit mercury to assume one of these favored geometries will, all other things being equal, be weaker binders than those that can [45,46]. The ligands mentioned in the previous paragraph are well suited to linear binding, so the new ligands were designed with a tetrahedral geometry in mind. Unlike the best previously reported ligands, these are alkyl rather than aromatic-based compounds and are highly flexible in order to allow for the tetrahedral geometry around Hg. Each has a three or four carbon backbone with a sulfide group on both ends and a two to four carbon alkyl arm attached to the each sulfide, with each arm ending in a thiol group. The ligand structures and abbreviated names are given in Fig. 2a–d. All but 3S2SH are new compounds; a synthesis of 3S2SH has been reported previously, but the compound was not utilized for mercury precipitation [47]. A key feature of these ligands is that they provide Hg with four sulfur bonds while remaining neutral, thereby reducing water solubility. When precipitated, the ligands “hide” the Hg atom in a hydrophobic environment. Our preliminary studies suggest that these ligands are comparable to the aromatic chelates as mercury precipitators and also yield highly stable mercury ligand precipitates.

2. Methods

2.1. Ligand syntheses

All reagents were purchased from Aldrich or Acros chemical companies and were reagent grade or better unless otherwise

noted. NMR measurements were taken on a Varian Gemini 200 MHz NMR Spectrometer. IR spectroscopy was performed using either a PerkinElmer model 1600 FT-IR spectrophotometer or a Nicolet Magna 560 FT-IR. GC–MS data were gathered using a Shimadzu QP2010S instrument, with a column flow of 1.71 mL He/min, a total flow of 39 mL He/min and a 25 min run (1.5 min at 150 °C, 2.5 min ramp to 275 °C, and 21 min at 275 °C).

3S2OH [47]. Sodium ethoxide (15.0 g, 220 mmol) was dissolved in approximately 200 mL of absolute ethanol, then 1,3-propanedithiol (1.00 mL, 109 mmol) was added. After this solution was stirred for a short time, 2-chloro-1-ethanol (15.0 mL, 224 mmol) was added and refluxed for 2 h. The solution was filtered and the ethanol was removed through vacuum evaporation. Methylene chloride was added to precipitate excess salt, the mixture was filtered a second time, and the methylene chloride was also removed through vacuum pumping. The solution was distilled between 179 and 182 °C under vacuum (0.5 mm Hg). Yield: 12.0 g (61.2 mmol), 56%. ^1H NMR (CDCl_3 , 200 MHz, δ ppm): 3.75 (t, 4H), 2.91 (s, 2H), 2.68 (m, 8H), 1.89 (p, 2H); ^{13}C NMR (CDCl_3 , 200 MHz, δ ppm): 60.7, 34.7, 30.4, 29.2; IR (thin film on NaCl plates, cm^{-1}): 3300(s, b), 2918(s), 1640(w), 1420(s), 1340(m), 1290(s), 1260(s), 1226(m), 1164(m), 1044(s), 1010(s), 942(m), 824(m), 762(m), 586(m), 534(m), 522(m); GC–MS: peak at RT = 4.52 min, m/z = 196 (M^+), purity by GC: 99.5%.

3S2SH [47]. 3S2OH (4.00 g, 20.4 mmol) was combined with thiourea (3.32 g, 43.6 mmol) in 10 mL concentrated HCl. The resulting solution was refluxed for 10 h. Potassium hydroxide (6.90 g, 123 mmol) in 40 mL of DI water was slowly added and the solution refluxed for three more hours. The resulting two-phase system was separated and the upper, aqueous phase extracted with ether. The ether was added to the original organic layer and the resulting mixture distilled between 159 and 161 °C at 0.5 mm Hg to yield 3S2SH. Yield: 2.51 g

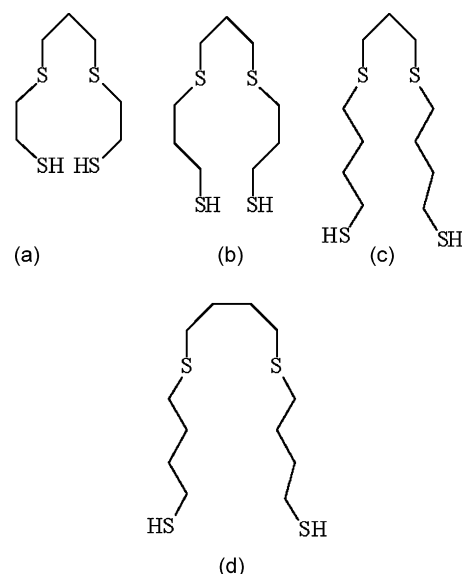


Fig. 2. Ligands studied in this work: (a) 3S2SH, (b) 3S3SH, (c) 3S4SH, (d) 4S4SH.

(54%). ^1H NMR (CDCl_3 , 200 MHz, δ ppm): 2.75 (m, 8H), 2.64 (t, 4H), 1.87 (p, 2H), 1.73 (t, 2H); ^{13}C NMR (CDCl_3 , 200 MHz, δ ppm): 36.06, 30.60, 29.26, 24.68; IR (thin film on NaCl plates, cm^{-1}): 2914(s), 2842(m), 2544(m), 1608(w), 1428(s), 1342(m), 1272(s), 1256(s), 1210(s), 1140(m), 964(m), 888(w), 848(m), 770(m), 698(s), 518(w); GC–MS: peak at RT = 5.43 min, m/z = 228 (M^+), purity by GC: 97.6%.

3S3SH. Cesium carbonate (40.2 g, 124 mmol) was suspended in approximately 250 mL of DMF (*N,N*-dimethylformamide) and allowed to stir for 20 min, followed by addition of propanedithiol (15.0 mL, 148 mmol). The resulting white suspension was stirred for 30 min. Diiodopropane (5.70 mL, 49.4 mmol) was then added dropwise using a dropping funnel and the mixture left to stir for 48 h. The DMF was removed by heating the suspension under vacuum. The remaining white solid was acidified with dilute HCl (a significantly exothermic reaction) and extracted with methylene chloride. The methylene chloride layer was distilled between 143 and 146 °C at 0.4 mm Hg, yielding the product. Yield: 4.30 g, 34%. ^1H NMR (CDCl_3 , 200 MHz, δ ppm): 1.32 (t, 2H), 1.69–1.98 (m, 6H), 2.47–2.75 (m, 12H); ^{13}C NMR (CDCl_3 , 200 MHz, δ ppm): 33.03, 30.52, 30.02, 28.99, 23.19; IR (thin film on NaCl plates, cm^{-1}): 2922(s), 2844(m), 2564(m), 1650(w), 1605(w), 1440(s), 1342(w), 1296(m), 1250(s), 1206(w), 1028(w), 958(w), 838(w), 758(w), 654(w); GC–MS: peak at RT = 16.236 min, m/z = 256 (M^+), purity by GC: 90.6%.

3S4SH. Cesium carbonate (75.0 g, 230 mmol) was suspended in DMF along with butanedithiol (45.0 mL, 384 mmol). This was stirred for 3 h, then dibromopropane (8.81 mL, 76.7 mmol) was slowly added in 100 mL DMF. The mixture was stirred for approximately 48 h, then the DMF was removed through heating under vacuum and after the residue was acidified, it was extracted with methylene chloride. When the organic layer was removed with vacuum, the residue was found to be a mixture of butanedithiol and 3S4SH. This was distilled between 149 and 156 °C at 0.4 mm Hg. Yield: 2.10 g (10%). ^1H NMR (CDCl_3 , 200 MHz, δ ppm): 2.39 (m, 12H), 1.75 (t, 2H), 1.55 (m, 10H); ^{13}C NMR (CDCl_3 , 200 MHz, δ ppm): 32.86, 31.40, 30.78, 29.22, 28.07, 24.12; IR (thin film on NaCl plates, cm^{-1}): 2930(s), 2848(s), 2546(w), 1708(w), 1638(w), 1436(s), 1342(w), 12.82(m), 1246(m), 1202(w), 1132(w), 1026(w), 994(w), 914(m), 840(w), 724(m), 652(w); GC–MS: peak at RT = 21.10 min, m/z = 284 (M^+), purity by GC: 97.2%.

4S4SH. Cesium carbonate (21.1 g, 64.9 mmol) was suspended in approximately 350 mL of DMF. To this was added technical grade (90%) butanedithiol (10.0 mL, 76.7 mmol). The suspension was stirred for 30 min, followed by the slow addition of diiodobutane (4.00 mL, 30.2 mmol) and 48 h of stirring at room temperature. The DMF was then removed by heating under vacuum and the residue acidified with dilute HCl. The acidic solution was extracted with methylene chloride and distilled between 181 and 189 °C at 0.4 mm Hg. Yield: 1 g (11%). ^1H NMR (CDCl_3 , 200 MHz, δ ppm): 2.52 (m, 12 H), 1.73 (m, 12H), 1.38 (t, 2H); ^{13}C NMR (CDCl_3 , 200 MHz, δ ppm): 32.82, 31.45, 31.32, 28.45, 28.01, 24.08; IR (thin film on NaCl plates, cm^{-1}): 2930(s), 2852(s), 2546(w), 1708(w), 1638(w), 1450(s),

1350(w), 1280(s), 1238(m), 1202(w), 1178(w), 1134(w), 1026(w), 1002(w), 914(m), 724(m), 652(w); GC–MS: peak at RT = 20.12 min, m/z = 298 (M^+), purity by GC: 97.3%.

2.2. Mercury precipitation studies

The ligands are not soluble in water in their thiol form and were used as solutions in THF (tetrahydrofuran). The ligand solutions were added to 30 ppm mercury solutions (mercuric chloride in water) in 1:1, 2:1, and 3:1 molar ratios. 4S4SH (0.0446 g, 0.150 mmol), 3S4SH (0.0422 g, 0.149 mmol), 3S3SH (0.0383 g, 0.150 mmol), and 3S2SH (0.0385 g, 0.167 mmol) were each added to separate 100 mL volumetric flasks, which were then filled to the line with THF. After vigorous stirring to ensure an even distribution of ligand in the solutions, a 1 mL, a 2 mL, and a 3 mL aliquot from each solution was added to 10 mL aliquots of a 30 ppm aqueous mercury solution (giving a total of 12 samples). Upon addition of ligand solution, all the mercury samples immediately became white and cloudy. Each sample was filtered with a 0.2 μm syringe filter prior to analysis via cold vapor atomic fluorescence spectroscopy (CVAFS). The CVAFS analysis was performed using a Vasal VI2000 atomic fluorescence spectrometer, calibrated using standard solutions to accurately measure mercury concentrations of between 0 and 30 ppb. Samples were initially run at a 200:1 dilution factor, then gradually analyzed at higher concentrations until they yielded values located upon the calibration curve. All readings were taken in triplicate or better to ensure reproducibility.

2.3. Mercury precipitate analysis

Mercury precipitation was repeated on a larger scale using mercury solutions of higher concentration so as to isolate sufficient precipitate for analysis. The precipitates were isolated for both a 1:1 and a 3:1 ratio of ligand to mercury and studied by mass spectral analysis (JEOL JMS-700T magnetic sector instrument), infrared spectroscopy (Nicolet Magna 560 FT-IR), elemental analysis, and thermogravimetric analysis. Elemental analyses were performed by Galbraith Laboratories in Knoxville, TN. The percentage of carbon and hydrogen was determined by combustion according to the ASTM D5373 and D5291 methods. The percentage of sulfur was determined by combustion according to ASTM D4239 Method B and ASTM D1552. There was a $\pm 0.5\%$ uncertainty in the measurements. TGA (thermogravimetric analyses) were performed by Edison Laboratories in Schenectady, NY, using a TA Instruments YGA2950, with a N_2 flow of 100 mL/min and a heating rate of 10 °C/min. The results are as follows.

3S2SH + HgCl_2 in a 1:1 ratio. Mercury chloride (1.19 g, 4.38 mmol) was dissolved in 35 mL of DI water. To this solution was added 3S2SH (1.00 g, 4.39 mmol) in 11 mL of HPLC grade THF. Upon addition of the ligand, a white precipitate immediately formed. The suspension was filtered to isolate the solid, identified as 3S2SHg·0.5 3S2SH. Yield: 0.369 g (0.683 mmol), 23%; IR (KBr pellet, cm^{-1}): 2935(s), 2823(m), 2523(w), 1634(w), 1427(m), 1407(m), 1331(w), 1303(s), 1265(m), 1204(m), 1144(m), 1018(w),

988(w), 900(m), 848(m), 801(w), 723(w), 692(w), 666(w), 634(w); mass spectrum: $m/z = 427$ (M^+); TGA: one mass loss from 190 to 345 °C of 83.83%, one mass loss from 345 to 410 °C of 13.19%. Anal. for 3S2SHg-0.5 3S2SH. Calcd. (found): C 23.28% (22.99%) H 4.09% (3.92%), S 35.52% (35.85%).

3S2SH+HgCl₂ in a 3:1 ratio. Mercury chloride (1.18 g, 4.21 mmol) was dissolved in 40 mL of DI water. To this solution was added 3S2SH (2.88 g, 12.6 mmol) in 11 mL of HPLC grade THF. Upon addition of the ligand, a white precipitate immediately formed. The suspension was filtered to isolate the solid, identified as 3S2SHg-1.4 3S2SH. Yield: 1.22 g (1.63 mmol), 39%, IR (KBr pellet, cm⁻¹): 2903(s), 2810(m), 2515(w), 1621(w), 1423(m), 1407(s), 1329(w), 1302(m), 1265(m), 1206(m), 1143(m), 1005(w), 959(w), 899(m), 847(m), 793(w), 723(w), 693(m), 663(w), 634(w); mass spectrum: $m/z = 427$ (M^+), TGA: one mass loss from 165 to 440 °C of 96.90%. Anal. for 3S2SHg-1.4 3S2SH. Calcd. (found): C 27.02% (33.56%), H 4.91% (4.63%), S 41.21% (41.49%).

3S3SH+HgCl₂ in a 1:1 ratio. Mercury chloride (1.59 g, 5.86 mmol) was dissolved in 40 mL of DI water. To this solution was added 3S3SH (1.50 g, 5.86 mmol) in 10 mL of HPLC grade THF. Upon addition of the ligand, a white precipitate immediately formed. The suspension was filtered to isolate the solid, identified as (3S3S)_{0.67}HgCl_{0.66}. Yield: 1.33 g (3.38 mmol), 58%, IR (KBr pellet, cm⁻¹): 2914(s), 2841(m), 2489(w), 1667(w), 1590(w), 1442(s), 1334(m), 1293(w), 1242(m), 1182(w), 1044(w), 1000(w), 953(w), 846(w), 740(m), 660(w); mass spectrum: $m/z = 455$ (M^+); TGA: one mass loss from 150 to 245 °C of 16.45%, one mass loss from 245 to 500 °C of 78.63%. Anal. for (3S3S)_{0.67}HgCl_{0.66}. Calcd. (found): C 18.39% (17.97%), H 2.92% (2.97%), S 21.82% (22.96%).

3S3SH+HgCl₂ in a 3:1 ratio. Mercury chloride (1.59 g, 5.86 mmol) was dissolved in 40 mL of DI water. To this solution was added 3S3SH (4.5 g, 17.6 mmol) in 20 mL of HPLC grade THF. Upon addition of the ligand, a white precipitate immediately formed. The suspension was filtered to isolate this solid, identified as 3S3SHg-1.3 3S3SH. Yield: 1.61 g (2.05 mmol), 35%, IR (KBr pellet, cm⁻¹): 2915(s), 2844(m), 2544(w), 1636(w), 1430(s), 1384(w), 1337(w), 1294(w), 1247(s), 1198(w), 1046(w), 955(w), 844(w), 741(w), 668(w); mass spectrum: highest mass at $m/z = 382$ (MH^+ minus (CH₂)₃S); TGA: one mass loss from 110 to 370 °C of 85.69%, one mass loss from 370 to 530 °C of 10.93%. Anal. for 3S3SHg-1.3 3S3SH. Calcd. (found): C 31.48% (31.34%), H 5.61% (5.33%), S 37.35% (37.59%).

3S4SH+HgCl₂ in a 1:1 ratio. Mercury chloride (1.43 g, 5.27 mmol) was dissolved in 40 mL of DI water. To this solution was added 3S4SH (1.50 g, 5.28 mmol) in 11 mL of HPLC grade THF. Upon addition of the ligand, a white precipitate immediately formed. The suspension was filtered to isolate this solid, identified as 3S4SHg-0.8 3S4SH. Yield: 1.81 g (2.56 mmol), 87%, IR (KBr pellet, cm⁻¹): 2919(s), 2854(m), 1634(w), 1430(s), 1339(w), 1307(m), 1248(m), 1190(m), 1113(w), 993(w), 913(w), 872(w), 738(m); mass spectrum:

highest mass at $m/z = 396$ (MH^+ minus (CH₂)₄S); TGA: one mass loss from 105 to 380 °C of 99.43%. Anal. for 3S4SHg-0.8 3S4SH. Calcd. (found): C 33.41% (33.51%), H 5.83% (5.72%), S 32.43% (32.19%).

3S4SH+HgCl₂ in a 3:1 ratio. Mercury chloride (1.43 g, 5.27 mmol) was dissolved in 40 mL of DI water. To this solution was added 3S4SH (4.50 g, 15.8 mmol) in 15 mL of HPLC grade THF. Upon addition of the ligand, a white precipitate immediately formed. The suspension was filtered to isolate this solid, identified as 3S4SHg-2.7 3S4SH. Yield: 1.56 g (1.25 mmol), 29.3%, IR (KBr pellet, cm⁻¹): 2919(s), 2854(m), 2510(w), 1625(w), 1431(s), 1340(w), 1308(m), 1251(m), 1190(m), 1048(w), 910(w), 872(w), 739(m), 668(w); mass spectrum: highest mass at $m/z = 396$ (MH^+ minus (CH₂)₄S); TGA: one mass loss from 100 to 380 °C of 98.51%. Anal. for 3S4SHg-2.7 3S4SH. Calcd. (found): C 39.06% (38.54%), H 6.99% (6.81%), S 37.92% (39.95%).

4S4SH+HgCl₂ in a 1:1 ratio. Mercury chloride (0.319 g, 1.17 mmol) was dissolved in 30 mL of DI water. To this solution was added 4S4SH (0.350 g, 1.17 mmol) in 10 mL of HPLC grade THF. Upon addition of the ligand, a white precipitate immediately formed. The suspension was filtered to isolate this solid, identified as 4S4SHg-0.1 4S4SH. Yield: 0.442 g (0.834 mmol), 78%, IR (KBr pellet, cm⁻¹): 2927(s), 2855(m), 1558(w), 1445(s), 1304(m), 1277(m), 1227(w), 1199(m), 1110(w), 983(w), 933(w), 900(w), 731(m), 668(w); mass spectrum: highest mass at $m/z = 411$ (MH^+ minus (CH₂)₄S); TGA: one mass loss from 130 to 220 °C of 54.77%, one mass loss from 220 to 415 °C of 44.40%. Anal. for 4S4SHg-0.1 4S4SH. Calcd. (found): C 30.18% (30.65%), H 5.11% (4.54%), S 26.86% (26.13%).

4S4SH+HgCl₂ in a 3:1 ratio. Mercury chloride (0.319 g, 1.17 mmol) was dissolved in 30 mL of DI water. To this solution was added 4S4SH (1.05 g, 3.52 mmol) in 11 mL of HPLC grade THF. Upon addition of the ligand, a white precipitate immediately formed. The suspension was filtered to isolate this solid, identified as 4S4SHg-1.9 3S4SH. Yield: 0.538 g (0.502 mmol), 43%, IR (KBr pellet, cm⁻¹): 2922(s), 2856(m), 2490(w), 1667(w), 1441(s), 1305(m), 1278(m), 1233(w), 1199(w), 1070(w), 1048(w), 730(w), 668(w); mass spectrum: highest mass at $m/z = 411$ (MH^+ minus (CH₂)₄S); TGA: one mass loss from 175 to 380 °C of 99.98%. Anal. for 4S4SHg-1.9 3S4SH. Calcd. (found): C 39.32% (39.77%), H 6.96% (6.89%), S 34.99% (34.32%).

2.4. Leaching studies

Between 0.20 and 0.26 g of each mercury ligand precipitate was added to two solutions, each containing one Metrepack pHHydrion buffer capsule (either pH 7.00 ± 0.02 or pH 2.00 ± 0.02) dissolved in 100 mL of DI water, then stirred vigorously, covered with parafilm, and left in a fume hood for 53 days. Three 10 mL aliquots from each sample were then filtered through a Corning 0.20 μm syringe filter. The resulting 48 filtrates (along with three DI water blanks) were analyzed for mercury concentration with a QuickTrace M-7500 cold vapor atomic absorption spectrometer.

Table 1
Results of the mercury precipitation Study, with comparison to commercial mercury precipitation agents [38]

Ligand	Ratio of ligand to mercury	Initial mercury concentration (ppb)	Mercury concentration after addition of ligand (ppb)	Percent of mercury removed
3S2SH	1:1	30,000	538	98.21
3S2SH	2:1	30,000	666	97.78
3S2SH	3:1	30,000	635	97.88
3S3SH	1:1	30,000	2,714	90.95
3S3SH	2:1	30,000	367	98.78
3S3SH	3:1	30,000	119	99.60
3S4SH	1:1	30,000	214	99.29
3S4SH	2:1	30,000	7	99.98
3S4SH	3:1	30,000	0	100.00
4S4SH	1:1	30,000	1,269	95.77
4S4SH	2:1	30,000	2,101	93.00
4S4SH	3:1	30,000	2,152	92.83
SDTC [38]	1:1	50,000	1,010	97.98
SDTC [38]	10% excess	50,000	690	98.62
STC [38]	1:1	50,000	8,590	82.82
STC [38]	10% excess	50,000	6,720	86.56
TMT [38]	1:1	50,000	18,070	63.86
TMT [38]	10% excess	50,000	15,150	69.7

3. Results and discussion

3.1. Ligand synthesis

The synthesis of relatively large dithioether dithiol ligands as described in this paper is not a trivial undertaking. A number of different methods were initially attempted to synthesize these compounds, but none proved to be satisfactory [48]. The scheme finally decided on, a straightforward S_N2 substitution with a dihalide and two dithiols, offered several potential side-products. To limit these undesired reactions, a large excess of dithiol was used and the dihalide was added dropwise to this dithiolate solution, thereby assuring that each dihalide molecule would see an excess of dithiol molecules. However, if a normal base (such as a sodium or potassium salt) was used to create the dithiolate, the reaction yielded none of the desired product. The reason for this was established by Ochrymowycz in 1974 [49]. In attempting to make thiocrown ethers by a similar methodology, he observed interchain cyclization during the reaction of dithiols with dihalides, creating a sulfonium intermediate that replaced the halide as the leaving group for the S_N2 attack. Literature precedent suggested, however, that S_N2 substitutions involving dithiols and dihalides could be successful if Cs_2CO_3 is used as the base [50]. This proved to be the case for the new dithioether dithiol ligands as well, although the yields remained low. It is believed that the large size of the cesium cation leads to sulfur–cesium bonds that can be considered especially ionic, making cesium thiolates more nucleophilic [51]. This leads to the thiolates reacting more rapidly, therefore, increasing the rate of halide displacement by metal thiolate compared to the rate of cyclization and yielding more of the desired product.

Once successful syntheses had been confirmed by initial GC–mass spectra, the ligands were readily purified by vacuum distillation. The characterization data for the compounds were largely unremarkable. Both proton and carbon NMR spectra showed all the peaks predicted for these molecules with the

proper integration. The IR spectra also showed the expected bands, particularly peaks between 2500 and 2600, where one would expect to find S–H stretching and peaks between 700 and 650, evaluated as C–S–C bending. The mass spectra showed molecular ions for all four ligands and the gas chromatographs indicated acceptable purity levels.

3.2. Mercury removal from water

The amount of mercury removed from 30 ppm aqueous solutions (Table 1) was found to vary significantly by ligand used, with 3S4SH giving the best overall result and 4S4SH giving the worst. In the case of the 3S4SH ligand, at all ratios, over 99% of the mercury was removed and with the 3:1 ratio, the mercury concentration in the filtrate was below the detection limits of the instrument used (below 0.5 ppb). It is possible that the relatively poor performance of the 4S4SH ligand was due to solubility issues, since this proved to be the least soluble (even in THF) of the set. It is noteworthy that with the addition of excess ligand, with the exception of 4S4SH, there was an increase with mercury removal with ligand size. This is consistent with the hypothesis that larger ligands can more easily assume a tetrahedral geometry around mercury and this leads to better binding. A possible reason that this trend was not observed for a 1:1 ratio of mercury to ligand will be put forward when the structure of the precipitates is discussed. With all ligands and ratios, however, at least 90% of the mercury was removed.

All of these ligands proved to be highly effective mercury removal agents. They are comparably effective to the commercially available DMDTC ligand (with a greater stability in the precipitates) and superior to the TC and TMT reagents [38]. In fact, the 3S4SH gave results that were as good and perhaps slightly better than the previously discussed aromatic ligands, which are arguably the best compounds currently known for precipitating mercury from water.

3.3. Mercury precipitates

To further investigate the nature and stability of the mercury precipitates, the 1:1 and 3:1 ratio reactions were repeated at much higher concentrations so as to generate enough precipitate to study. As before, white precipitate appeared immediately upon addition of the ligand in THF to the mercury solutions. The precipitates (which were insoluble in both water and organic solvents) were isolated by filtration and analyzed by IR, mass spectroscopy, thermogravimetric analysis (TGA), and elemental analyses (%C, H, and S).

The mass spectra clearly showed the presence of ligand bound to the mercury. The highest mass peak generally corresponded to a mercury atom with either an entire ligand attached (the precipitates made from 3S2SH and 3S3SH in the 1:1 ratio) or a mercury atom with one ligand minus a small sulfur ring ($(\text{CH}_2)_3\text{S}$ for the 3S3SH 3:1 precipitate $(\text{CH}_2)_4\text{S}$ for the others). The TGAs showed a steady loss of essentially all of the compound's mass for all the precipitates. The mass loss occurred over different temperature ranges for each ligand used; however, for a given ligand the decomposition occurred in approximately the same temperature range for both the 1:1 and 3:1 ratios. Although for some of the compounds there were small changes in the slope of the TGA curve during the decomposition, these did not appear to indicate truly separate weight loss events. In total, this evidence suggests a distinct similarity between the precipitates resulting from the 1:1 ratio and the 3:1 ratio.

However, much of the other data suggested that the precipitates' composition was more complex than just one ligand bound to one mercury. Many of the IR spectra showed a slight S–H stretching peak, suggesting that not all of the terminal sulfurs were bound to mercury. The elemental analyses also pointed to differences between the 1:1 and 3:1 precipitate and proved most useful for characterizing these compounds. In the case of every precipitate, except that resulting for 3S3SH ligand in a 1:1 ratio with mercury, the C, H, and S% was higher than predicted for a 1:1 ligand to metal stoichiometry. Furthermore, the reaction involving excess ligand always produced precipitates with a higher C, H, and S% than the reactions with a stoichiometric amount of ligand. The analysis suggests that the ligand is present in the precipitates in a greater than stoichiometric amount, except in the case of the previously mentioned 3S3SH compound, where the composition agrees with a ratio of approximately two ligand to three mercury. The presence of this extra, still fully protonated, ligand in the majority of the precipitates also accounts for the SH peaks observed in the IR spectra. It is worth noting that the data for the 4S4SH precipitates are not remarkably different than the others (with the exception of the TGA), supporting the idea that its poor performance was due to solubility issues rather than an inherent difference in its reactivity with mercury.

Although the precipitates can hardly be assigned a definitive structure on the basis of these data, it does seem reasonable to conclude that excess ligand is bound to the primary mercury ligand precipitate (although we cannot definitely say how the excess ligand is bound). This interpretation is consistent with the majority of the characterization data and the observed

results, namely that a greater mercury removal was seen when excess ligand was added. The exception to this is the TGA of the 4S4SH precipitates, in which the mass loss begins at a higher temperature in the 3:1 solid than in the 1:1 precipitate; this is the reverse of what is seen for the others and what would be predicted. However, while perplexing, this does not rule out the presence of excess ligand with the precipitate, it merely suggests its association is more complex than it might otherwise appear.

If there is excess ligand in the precipitate, then those molecules are not available to bind a mercury atom and a greater than 1:1 stoichiometry is desirable for quantitative removal. In the previous section it was noted that, when a greater than stoichiometric amount of ligand was added, and excepting the poor-performing 4S4SH, larger ligands yielded greater mercury removal. The excess ligand in the precipitate explains why that trend did not hold true for a 1:1 ligand to mercury ratio; that is an insufficient amount of ligand to precipitate all the mercury. Therefore, if these ligands are utilized for mercury remediation, an excess of ligand should be used to maximize the precipitation.

3.4. Leaching studies

To examine the long-term stability of the precipitates, leaching studies were performed. Acidic as well as neutral water was used for the leaching studies because mercury contaminated waters, such as mine runoffs, are often acidic. Overall, the results (Table 2) are very positive; in only one sample was the average concentration greater than 10 ppb and the majority of the samples contained less than 1 ppb mercury. A number of samples (once corrected for the slight background mercury in the blanks) contained no mercury at all. It appears that leaching

Table 2
Results of the leaching study

Precipitate studied (named by ligand and ratio of ligand to mercury used to form precipitate)	pH	Hg concentration after leaching study (ppb)
3S2SH 1:1	2	0.01
	7	3.48
3S2SH 3:1	2	0.11
	7	5.60
3S3SH 1:1	2	0.12
	7	14.66
3S3SH 3:1	2	0.00
	7	0.12
3S4SH 1:1	2	0.00
	7	0.41
3S4SH 3:1	2	0.00
	7	0.00
4S4SH 1:1	2	0.00
	7	0.00
4S4SH 3:1	2	0.00
	7	0.00

of mercury from the precipitates will not be a major problem for these ligands. It is interesting to note that for several of the compounds, there was greater leaching in the neutral solution than in the acidic one. While initially counterintuitive, this suggests that the major mechanism for leaching in these compounds is not acidic attack on the mercury sulfur bond. Therefore, these ligands have some potential for *in situ* remediation of acidic waste streams.

4. Conclusions

The new ligands appear to perform as intended and are competitive with the previously published aromatic compounds. Not only does 3S4SH remove mercury near quantitatively; the resulting precipitates appear to be stable. The relatively lesser removal of mercury by the 4S4SH ligand appears to be a result of its lower solubility in a water/THF mix, not any inherent difference in its chemistry, as indicated by the analysis of the precipitates and the leaching studies. Furthermore, it must be kept in mind that these results were generated by simply adding unmodified ligand in an organic solvent to the mercury solution. Unlike the commercial reagents mentioned above, the new ligands were not used as water-soluble group 1 metal thiolates. The insoluble thiol ligands are, in and of themselves, highly effective mercury removal agents for any system in which they can be safely added with an organic cosolvent. It would be expected that a water-soluble version of these compounds might be even more effective. Our current research is being directed towards the development of such a water-soluble variant and its testing on more complex samples (such as those containing potentially interfering ions such as Ca^{2+} , Mg^{2+} , and $\text{Fe}^{2+}/\text{Fe}^{3+}$).

References

- [1] O. Malm, Gold mining as a source of mercury exposure in the Brazilian Amazon, *Environ. Res.* 77 (1998) 73–78.
- [2] A. Boudou, R. Maury-Brachet, M. Coquery, G. Durrieu, D. Cossa, Synergic effect of gold mining and damming on mercury contamination in fish, *Environ. Sci. Technol.* 39 (2000) 2448–2454.
- [3] N. Pirrone, I. Allegrini, G.J. Keeler, J.O. Nriagu, R. Rossmann, J.A. Robbins, Historical atmospheric mercury emissions and depositions in North America compared to mercury accumulations in sedimentary records, *Atmos. Environ.* 32 (1998) 929–940.
- [4] J.L. Kambey, A.P. Farrell, L.I. Bendell-Young, Influence of illegal gold mining on mercury levels in fish of North Sulawesi's Minahasa Peninsula (Indonesia), *Environ. Pollut.* 114 (2001) 299–302.
- [5] J.S. Kinsey, F.R. Anscombe, S.E. Lindberg, G.R. Southworth, Characterization of the fugitive mercury emissions at a chlor-alkali plant: overall study design, *Atmos. Environ.* 38 (2004) 633–641.
- [6] J.S. Kinsey, J. Swift, J. Bursey, Characterization of fugitive mercury emissions from the cell building at a US chlor-alkali plant, *Atmos. Environ.* 38 (2004) 623–631.
- [7] M. Futatsuka, T. Kitano, M. Shono, Y. Fukuda, K. Ushijima, T. Inaoka, M. Nagano, J. Wakamiya, K. Miyamoto, Health surveillance in the population living in a methyl mercury-polluted area over a long period, *Environ. Res.* 83 (2000) 83–92.
- [8] D. Seyferth, Phenyl(trihalomethyl)mercury compounds. Exceptionally versatile dihalocarbene precursors, *Acc. Chem. Res.* 5 (1972) 65–74.
- [9] E.M. Sunderland, G.L. Chmura, An inventory of historical mercury emissions in Maritime Canada: implications for present and future contamination, *Sci. Total Environ.* 256 (2000) 39–57.
- [10] Y.E. Yudovich, M.P. Ketris, Mercury in coal: a review. Part 2. Coal use and environmental problems, *Int. J. Coal Geol.* 62 (2005) 135–165.
- [11] C. Holden, Death by lab poisoning, *Science* 276 (1997) 1797.
- [12] D.W. Boening, Ecological effects, transport, and fate of mercury: a general review, *Chemosphere* 40 (2000) 1335–1351.
- [13] P.B. Tchounwou, W.K. Ayensu, N. Ninashvili, D. Sutton, Review: environmental exposure to mercury and its toxicopathologic implications for public health, *Environ. Toxicol.* 18 (2003) 149–175.
- [14] F. Bakir, S.F. Damluji, L. Amin-Zaki, M. Murtadha, A. Khalidi, Y. Al-Rawi, S. Tikriti, H.I. Dhahir, T.W. Clarkson, J.C. Smith, R.A. Doherty, Methylmercury poisoning in Iraq, *Science* 181 (1973) 230–241.
- [15] N. Auger, O. Kofman, T. Kosatsky, B. Armstrong, Low-level methylmercury exposure as a risk factor for neurologic abnormalities in adults, *NeuroToxicology* 26 (2005) 149–157.
- [16] T.W. Clarkson, Human toxicology of mercury, *J. Trace Elem. Exp. Med.* 11 (1998) 303–317.
- [17] M. Harada, J. Nakanishi, E. Yasoda, M.C.N. Pinheiro, T. Oikawa, G.A. Guimaraes, B. Cardoso, T. Kizaki, H. Ohno, Mercury pollution in the Tapajos River basin, Amazon, *Environ. Int.* 27 (2001) 285–290.
- [18] F.M.M. Morel, A.M.L. Kraepiel, M. Amyot, The chemical cycle and bioaccumulation of mercury, *Annu. Rev. Ecol. Syst.* 29 (1998) 543–571.
- [19] A.R. Hutchison, D.A. Atwood, Mercury pollution and remediation: the chemist's response to a global crisis, *J. Chem. Crystallogr.* 33 (2003) 631–645.
- [20] A.C.P. Heaton, C.L. Rugh, N.J. Wang, R.B. Meagher, Physiological responses of transgenic merA-tobacco (*Nicotiana tabacum*) to foliar and root mercury exposure, *Water Air Soil Pollut.* 161 (2005) 137–155.
- [21] F.N. Moreno, C.W.N. Anderson, R.B. Stewart, B.H. Robinson, Mercury volatilisation and phytoextraction from base-metal mine tailings, *Environ. Pollut.* 136 (2005) 341–352.
- [22] E. Pilon-Smits, M. Pilon, Breeding mercury-breathing plants for environmental cleanup, *Trends Plant Sci.* 5 (2000) 235–236.
- [23] S.G. Riddle, H.H. Tran, J.G. Dewitt, J.C. Andrews, Field, laboratory, and X-ray absorption spectroscopic studies of mercury accumulation by water hyacinths, *Environ. Sci. Technol.* 36 (2002) 1965–1970.
- [24] C.L. Rugh, Mercury detoxification with transgenic plants and other biotechnological breakthroughs for phytoremediation, *In Vitro Cell Dev. Biol. Plant* 37 (2001) 321–325.
- [25] A.E. Gash, A.L. Spain, L.M. Dysleski, C.J. Flaschenriem, A. Kalaveshi, P.K. Dorhout, S.H. Strauss, Efficient recovery of elemental mercury from Hg(II)-contaminated aqueous media using a redox-recyclable ion-exchange material, *Environ. Sci. Technol.* 32 (1998) 1007–1012.
- [26] W. Hollerman, L. Holland, D. Ila, J. Hensley, G. Southworth, T. Klasson, P. Taylor, J. Johnston, R. Turner, Results from the low-level mercury sorbent test at the oak ridge Y-12 plant in Tennessee, *J. Hazard. Mater.* 68 (1999) 193–203.
- [27] M.F. Yardim, T. Budinova, E. Ekinci, N. Petrov, M. Razvigorova, V. Minkova, Removal of mercury (II) from aqueous solution by activated carbon obtained from furfural, *Chemosphere* 52 (2003) 835–841.
- [28] K. Kadirvelu, M. Kavipriya, C. Karthika, N. Vennilamani, S. Pattabhi, Mercury(II) adsorption by activated carbon made from sago waste, *Carbon* 42 (2004) 745–752.
- [29] A.M. Starvin, T.P. Rao, Removal and recovery of mercury(II) from hazardous wastes using 1-(2-thiazolylazo)-2-naphthol functionalized activated carbon as solid phase extractant, *J. Hazard. Mater.* 113 (2004) 75–79.
- [30] M.C. Dujardin, C. Vaze, I. Vroman, Ion-exchange resins bearing thiol groups to remove mercury, *React. Funct. Polym.* 43 (2000) 123–132.
- [31] J.M. Monteagudo, M.J. Ortiz, Removal of inorganic mercury from mine waste water by ion exchange, *J. Chem. Technol. Biotechnol.* 75 (2000) 767–772.
- [32] M.E. Mahmoud, Selective solid phase extraction of mercury(II) by silica gel-immobilized-dithiocarbamate derivatives, *Anal. Chim. Acta* 398 (1999) 297–304.
- [33] C. Liu, Y. Huang, N. Naismith, J. Exonomy, J. Talbott, Novel polymeric chelating fibers for selective removal of mercury and cesium from water, *Environ. Sci. Technol.* 37 (2003) 4261–4268.
- [34] T.F. Baumann, J.G. Reynolds, G.A. Fox, Polymer pendant crown thioethers: synthesis, characterization and Hg^{2+} extraction studies of polymer-

- supported thiacrowns ([14]aneS₄ and [17]aneS₅), *React. Funct. Polym.* 44 (2000) 111–120.
- [35] A. Chojnacki, K. Chojnacka, J. Haffmann, H. Gorecki, The application of natural zeolites for mercury removal: from laboratory tests to industrial scale, *Miner. Eng.* 17 (2004) 933–937.
- [36] R.I. Nooney, M. Kalyanaraman, G. Kennedy, E.J. Maginn, Heavy metal remediation using functionalized mesoporous silicas with controlled macrostructure, *Langmuir* 17 (2001) 528–533.
- [37] F. Tassel, J. Rubio, M. Misra, B.C. Jena, Removal of mercury from gold cyanide solution by dissolved air flotation, *Miner. Eng.* 10 (1997) 803–811.
- [38] M.M. Matlock, K.R. Henke, D.A. Atwood, Effectiveness of commercial reagents for heavy metal removal from water with new insights for future chelate designs, *J. Hazard. Mater.* 92 (2002) 129–142.
- [39] K.R. Henke, D. Robertson, M.K. Krepps, D.A. Atwood, Chemistry and stability of precipitates from aqueous solutions of 2,4,6-trimercaptotriazine, trisodium salt, nonahydrate (TMT-55) and mercury(II) chloride, *Water Res.* 34 (2000) 3005–3013.
- [40] M.M. Matlock, B.S. Howerton, D.A. Atwood, Irreversible precipitation of mercury and lead, *J. Hazard. Mater.* 84 (2001) 73–82.
- [41] M.M. Matlock, B.S. Howerton, M.A. van Aelstyn, F.L. Nordstrom, D.A. Atwood, Advanced mercury removal from gold leachate solutions prior to gold and silver extraction: a field study from an active gold mine in Peru, *Environ. Sci. Technol.* 36 (2002) 1636–1639.
- [42] K.M. Zaman, L.Y. Blue, F.E. Huggins, D.A. Atwood, Cd, Hg, and Pb compounds of benzene-1,3-diamidoethanethiol (BDETH₂), *Inorg. Chem.* 46 (2007) 1975–1980.
- [43] C.E. Holloway, M. Melnik, Crystal Structures of mercury coordination complexes, *Main Group Met. Chem.* 17 (1994) 799–885.
- [44] C.E. Holloway, M. Melnik, Mercury organometallic compounds: classification and analysis of crystallographic and structural data, *J. Organomet. Chem.* 495 (1995) 1–31.
- [45] W.N. Setzer, Y. Tang, G.J. Grant, D.G. VanDerveer, Synthesis and complexation studies of mesocyclic and macrocyclic polythioethers. 8. Synthesis and X-ray crystal structures of heavy-metal complexes of 1,5,9,13-tetrathiacyclohexadecane, *Inorg. Chem.* 30 (1991) 3652–3656.
- [46] R.D. Bach, H.B. Vardhan, A mercury-199 NMR study of the complexation of methylmercury with thia-crown ethers. The absence of a macrocyclic ligand effect, *J. Org. Chem.* 51 (1986) 1609–1610.
- [47] W. Rosen, D.H. Busch, Nickel(II) complexes of cyclic tetradentate thioethers, *J. Am. Chem. Soc.* 91 (1969) 4694–4697.
- [48] A.R. Hutchison, The design and synthesis of novel chelates for the precipitation of mercury, Doctoral Dissertation, The University of Kentucky, Lexington, KY, 2007.
- [49] L.A. Ochrymowycz, C.P. Mak, J.D. Michna, Synthesis of macrocyclic polythiaethers, *J. Org. Chem.* 39 (1974) 2079–2084.
- [50] J. Buter, R.M. Kellogg, Synthesis of sulfur-containing macrocycles using cesium thiolates, *J. Org. Chem.* 46 (1981) 4481–4485.
- [51] J.A. Huheey, E.A. Keiter, R.L. Keiter, *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed., Harper Collins College Publishers, New York, NY, 1993.