

Bis(*n*-alkanethiolato)mercury(II) Compounds, Hg(SC_{*n*}H_{2*n*+1})₂ (*n* = 1 to 10, 12): Preparation Methods, Vibrational Spectra, GC/MS Investigations, and Exchange Reactions with Diorganyl Disulfides[†]

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Several preparative routes to bis(*n*-alkanethiolato)mercury(II) compounds of the general composition Hg(SC_{*n*}H_{2*n*+1})₂ for *n* = 1–10, 12 (compounds **1**–**11**, respectively) are presented, including the reaction of mercury(II) iodide with *n*-alkanethiols and triethylamine as an auxiliary base, as well as the reaction of mercury(II) chloride with trimethylsilyl methyl sulfide as an example for this particular type of exchange reaction using trimethylsilyl sulfides as thiolate transferring reagents. With respect to the possibility of mobilizing these compounds into the environment under special natural surroundings, as for example found in some natural gas reservoirs, the reactivity of the title compounds toward excess di-*n*-alkyl disulfides leading to the exchange of the thiolate functional groups of both the mercury compounds and the disulfides is investigated. Equilibration reactions of specifically stoichiometric amounts of Hg(SC₃H₇)₂ (**3**) and C₇H₁₅SSC₇H₁₅, as well as Hg(SC₇H₁₅)₂ (**7**) and C₃H₇SSC₃H₇ are investigated in more detail using the coupling of gas chromatography and mass spectrometry (GC/MS). The FT-IR and FT-Raman spectroscopic data of the solid title compounds are given and discussed. Assignments of ν_s(Hg–S) and ν_{as}(Hg–S) stretchings, as well as δ(C–S–Hg) and δ(S–Hg–S) bendings are reported and discussed in comparison to literature data. The spectroscopic data suggest mercury to be two-coordinated in all studied compounds with the exception of Hg(SC₄H₉)₂ (**4**). This particular compound obviously contains a four-coordinated central mercury atom. The title compounds were analyzed by means of GC/MS, which indicated that the compounds (i) decompose at elevated temperatures, mainly to form mercury and the corresponding disulfide, and (ii) are monomer in the gas phase.

Introduction

Despite the fact that bis(*n*-alkanethiolato)mercury(II) compounds of the general composition Hg(SR)₂ have been long known,^{1–5} there still remain a lot of unsolved domains concerning their chemistry and spectroscopic behavior. With respect to the chemistry of mercury that has attracted considerable interest, due to the extremely high toxicity of the metal itself, its inorganic compounds, and even more so its organic compounds to living systems,^{6–12} we have investigated several preparative routes to a series of homoleptic compounds of the general composition Hg(SC_{*n*}H_{2*n*+1})₂ for *n* = 1–10, 12 (compounds **1**–**11**, respectively).

Because of scarce and even poor structural data (further refinements of the structural data of some compounds seem to be necessary) available for these compounds,^{13–19} the solid-state vibrational spectra are of special interest, too,²⁰ so much the more as some controversial discussions with respect to the assignments of fundamental vibrations still exist.^{21,22a} In addition, ¹H NMR spectroscopic data of these homoleptic compounds do not contribute spectacular knowledge.²³ Moreover, the reactivity of the title compounds toward thiolate functional

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groups is of particular importance, due to the great affinity of sulfur for mercury.^{1–5} Especially its affinity for thiols is generally used to remove mercury from the body when poisoned by mercury and its compounds.^{24–26} Furthermore, similar compounds play an important role in the biochemistry of mercury.^{19,27–29} Previously, some of us reported the reaction of mercury with diorganyl disulfides, (CH₃)₂S₂ and (C₆H₅)₂S₂, to result in the formation of the corresponding bis(*n*-organothiolato) mercury(II) derivatives.^{23,30} Generally, these reactions play a pivotal role in some natural systems because of their ability to mobilize and transport mercury into the environment.^{6–12}

The present work will focus on the reactivity of the title compounds toward organic disulfides, which leads to the exchange of the thiolate functional groups of both the mercury compounds and the disulfides. Generally, the understanding of such exchange reactions provides detailed insight into the fundamental processes of mobilization and transport mechanisms of these environmentally important compounds.

Moreover, we extended our investigations on the IR and Raman spectra of these compounds in the solid state to allow comparisons to be made of both the title compounds with each other and the collected data with those already published.

Experimental Section

All solvents and chemicals were reagent grade and used as received. FT-Raman spectra were recorded with a Raman module FRA 106 (Nd: YAG laser, 1064 nm, <200 mW) attached to a Bruker IFS 66v interferometer. FT-IR spectra were done with KBr and CsI pellets and/or Nujol grindings between PE plates (the latter was done to make sure that possible exchange reactions of KBr and CsI with the title compounds do not seriously affect the IR spectra, as well as to obtain IR spectra at frequencies below 200 cm⁻¹) with the interferometer (in the range 500–50 cm⁻¹) and a Perkin-Elmer Paragon 1000 FT-IR spectrometer (in the range 4000–200 cm⁻¹), respectively.

Gas chromatographic investigations (GC) were performed using a Hewlett-Packard Model 5890 Series II instrument, equipped with a 30 m DB 5 capillary column (i.d. 0.25 mm) and a Hewlett-Packard flame photometric detector (initial temperature 35 °C and ramping to 320 °C at 5 °C/min). Injector and detector temperatures were set to 280 °C, and the helium carrier-gas flow was 1 mL/min. Gas chromatography–mass spectrometry (GC/MS) was performed using a Hewlett-Packard Model 6890 A instrument, equipped with a 30 m HP-5MS capillary column (i.d. 0.25 mm) and a Hewlett-Packard 5973 MS detector (initial temperature 40 °C and ramping to 290 °C at 5 °C/min). The injector temperature was set to 250 °C and the ion source to 230 °C, and the helium carrier-gas flow was 1 mL/min. Mass spectra were obtained by electron ionization at 70 eV; resolution, $\Delta m = 1$; scan range, 45–500 or 45–750; scan speed, 1.66 scans/min. The injector system of the GC/MS was a split/splitless inlet.

It has to be taken into account that the high temperatures applied during the GC investigations contribute to both the decomposition of

the title compounds (cf. Identification of Hg(SR)₂ ...) as well as an acceleration of the exchange processes of the title compounds with the diorganyl disulfides on the GC injector system, thus influencing the equilibration. That is the reason these exchange reactions can only be considered qualitatively. Nevertheless, the exchange reactions proceed already at ambient temperatures, as documented in the different total ion chromatograms (Figure 1) recorded during the equilibration experiments.

Elemental analyses (C, H) were performed with a Heraeus elemental analyzer, and sulfur was analyzed according to the method of Schöniger.³¹ DSC and TG measurements were obtained using a 910 differential scanning calorimeter, a 951 thermogravimetric analyzer, and a Thermal Analyst 2100 for data analysis.

Preparations. Caution! Because of the toxicity of mercury and its compounds all reactions were carried out in Schlenk tubes. The contact of mercury compounds with metallic apparatuses can lead to parasitic reactions. Therefore, the use of metallic apparatuses was strictly avoided with the exception of GC and GC/MS experiments (syringes and needles).

Analytical data, preparative methods, and yield of the title compounds are given in Table 1.

General Procedures for the Preparation of Bis(*n*-alkanethiolato)mercury(II) Compounds, Hg(SC_{*n*}H_{2*n*+1})₂, (*n* = 1–10, 12). (a) Reactions of *n*-Alkanethiols, (*n* = 1–10, 12) with Mercury(II) Nitrate. *n*-Alkanethiol (2 equiv) was added to a solution of mercury(II) nitrate (1 equiv) in 30 mL (1, 3–9, 11) or 120 mL (2, 10) portions of 1:1 ethanol/water (cf. Table 1). A voluminous precipitate immediately formed. After stirring for 12 h in the dark, the colorless crystals were collected by filtration and washed twice with cold absolute ethanol. After removal of the solvent in vacuo the compounds were used without further purification.

(b) Reactions of *n*-Alkanethiols, (*n* = 2–5, 8, 10, 12) and Triethylamine with Mercury(II) Iodide.¹⁸ *n*-Alkanethiol (2.2 equiv) was added to a solution of mercury(II) iodide (1 equiv) in 30 mL (2–5, 10, 11) or 90 mL (8) portions of absolute ethanol (cf. Table 1). A voluminous precipitate immediately formed that became microcrystalline after adding triethylamine (2.2 equiv) to the reaction mixture. After filtration, the precipitate was washed twice with water. The further workup of the reaction products followed the procedure described in part a.

(c) Reactions of *n*-Alkanethiols, (*n* = 2, 5, 6, 8) with Hg(SC_{*n*}H_{2*n*+1})₂.¹⁸ *n*-Alkanethiol (2.2 equiv) was added to a suspension of bis(*n*-alkanethiolato)mercury(II) (1 equiv) in 30 mL of absolute ethanol (cf. Table 1). After stirring for 12 h in the dark at ambient temperature, a solution formed, which was evaporated to dryness. The remaining colorless precipitate was washed twice with cold absolute ethanol and used without further purification after removal of the solvent in vacuo. The progress of the reaction was documented by means of GC.

(d) Reactions of Organic Disulfides, (C_{*n*}H_{2*n*+1})₂S₂, (*n* = 1–3, 9, 10) with Hg(SC_{*n*}H_{2*n*+1})₂. Di-*n*-alkyl disulfide (1.1 equiv) was added to a suspension of bis(*n*-alkanethiolato)mercury(II) (1 equiv) in 30 mL of absolute ethanol (cf. Table 1). After stirring for 12 h in the dark at 50 °C, a solution formed, which was treated as described in part c, provided that the exchanged disulfide has a lower boiling point than the exchanging disulfide. Otherwise the compound was collected with lower yield by cooling the solution. The progress of the reaction was followed by means of GC.

(e) Redox Reactions of Organic Disulfides (C_{*n*}H_{2*n*+1})₂S₂, (*n* = 1–3, 7, 8) with Mercury.^{23,30} Di-*n*-alkyl disulfide (5 mL) was stirred with mercury for 2–4 weeks in the dark at temperatures slightly higher than ambient temperature. A grayish precipitate resulted. Then 20 mL of CH₂Cl₂ was added to the reaction mixture. Excess mercury slowly separated. The solution was decanted and evaporated to dryness. The white precipitate was treated as described in part c.

(f) Reactions of HgCl₂ with Trimethylsilyl methyl sulfide, [(CH₃)₃SiSCH₃]. Trimethylsilyl methyl sulfide (11.1 g, 9.25 mmol) was added to a suspension of 1.14 g (4.20 mmol) of mercury(II) chloride in 30 mL of CH₂Cl₂. After stirring of the reaction mixture at ambient

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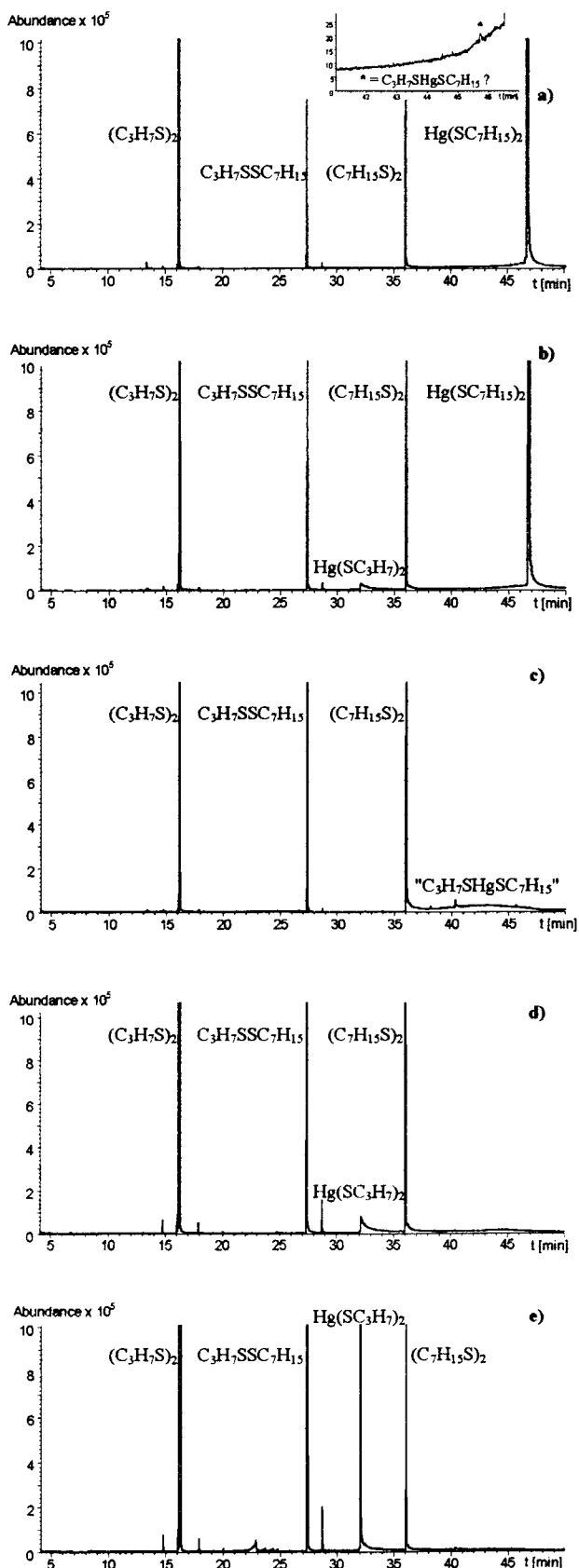


Figure 1. Total ion chromatograms (tics) of equilibrium 7 recorded after a reaction period of (a) 48 h, (b) 216 h, (c) 360 h, (d) 528 h (after addition of excess (C₃H₇S)₂ to the reaction mixture after a reaction time of 384 h), and (e) 696 h.

temperature for 12 h, a colorless solution formed, which was evaporated to dryness. The workup of the remaining colorless precipitate followed the procedure described in part a.

Equilibration Experiments. (a) 3 and C₇H₁₅SSC₇H₁₅. Compound 3 (110 mg, 0.314 mmol) was dissolved in a mixture of 82.2 mg (0.314 mmol) of C₇H₁₅SSC₇H₁₅ in 7 mL of CH₂Cl₂. A solution immediately formed which was stirred at ambient temperature in the dark. After 48, 216, and 360 h, 1 μL samples of the solution were injected into the GC/MS device. The following compounds could be detected using GC/MS: (1) C₃H₇SSC₃H₇ (M⁺ = 150), (2) C₃H₇SSC₇H₁₅ (M⁺ = 206), (3) 3 (M⁺ = 350; Hg isotope pattern), (4) C₇H₁₅SSC₇H₁₅ (M⁺ = 262), (5) C₃H₇SHgSC₇H₁₅ (12) (M⁺ = 406; Hg isotope pattern), and (6) 7 (M⁺ = 462; Hg isotope pattern). Additionally, the following compounds were formed in very low concentrations as decomposition products, mainly caused by the high temperatures applied during the GC/MS investigations:¹⁸ (7) C₃H₇SC₃H₇ (M⁺ = 118), (8) C₃H₇SSC₃H₇ (M⁺ = 182), (9) C₇H₁₅SC₇H₁₅ (M⁺ = 230), and (10) C₇H₁₅SSC₇H₁₅ (M⁺ = 294). After 384 h, excess C₇H₁₅SSC₇H₁₅ was added to the reaction mixture. Further GC/MS chromatograms were recorded after 528 and 696 h, respectively.

(b) 7 and C₃H₇SSC₃H₇. Compound 7 (201 mg, 0.434 mmol) was dissolved in a mixture of 65.2 mg (0.434 mmol) of C₃H₇SSC₃H₇ in 10 mL CH₂Cl₂. After stirring at ambient temperature in the dark, the mercury compound was completely dissolved. After 48, 216, and 360 h, 1 μL samples of the solution were injected into the GC/MS device. The following compounds could be found using GC/MS: (1) C₃H₇SSC₃H₇ (M⁺ = 150), (2) C₃H₇SSC₇H₁₅ (M⁺ = 206), (3) 3 (M⁺ = 350; Hg isotope pattern), (4) C₇H₁₅SSC₇H₁₅ (M⁺ = 262), (5) 12 (M⁺ = 406; Hg isotope pattern), and (6) 7 (M⁺ = 462; Hg isotope pattern). The same decomposition products as in part a could be found. After 384 h, excess C₃H₇SSC₃H₇ was added to the reaction mixture. Further GC/MS chromatograms were recorded after 528 and 696 h, respectively.

(c) 3, 7, C₇H₁₅SSC₇H₁₅, and C₃H₇SSC₃H₇ (Control Experiment). Compounds 3 (78.0 mg, 0.222 mmol) and 7 (109 mg, 0.235 mmol) were dissolved in a mixture of 35.4 mg (0.235 mmol) C₃H₇SSC₃H₇ and 38.4 mg (0.222 mmol) of C₇H₁₅SSC₇H₁₅ in 12 mL of CH₂Cl₂. A solution immediately formed which was stirred at ambient temperature in the dark. After 48, 216, 360, 528, and 696 h, 1 μL samples of the solution were injected into the GC/MS device. The following compounds could be detected by their mass spectra: (1) C₃H₇SSC₃H₇ (M⁺ = 150), (2) C₃H₇SSC₇H₁₅ (M⁺ = 206), (3) 3 (M⁺ = 350; Hg isotope pattern), (4) C₇H₁₅SSC₇H₁₅ (M⁺ = 262), (5) 12 (M⁺ = 406; Hg isotope pattern), and (6) 7 (M⁺ = 462; Hg isotope pattern). The same decomposition products as in part a could be found.

Results and Discussion

Synthesis. Bis(organothiolato)mercury(II) compounds can be prepared by several methods. The most common preparation is achieved by the reaction of Hg(CN)₂ with 2 equiv of RSH.^{5,32–34} Instead of Hg(CN)₂, other starting compounds are often used, such as HgO,^{1–3,35} Hg(ClO₄)₂,¹⁷ Hg(OAc)₂,^{36,37} Hg[N(SiCH₃)₂]₂,³⁸ and Hg(NO₃)₂,²³ respectively. In addition, the reaction of HgCl₂ with alkali mercaptides^{23,38,39} as well as photochemically⁴⁰ or electrochemically⁴¹ initiated redox reactions starting from mercury and organic disulfides are known.

With respect to the focus of these investigations on the mobilization of mercury, it was of particular interest to get information about the reactivity of Hg(SR)₂ compounds toward organic thiols¹⁸ and organic disulfides, respectively. Therefore,

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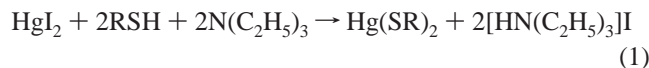
Table 1. Analytical Data, Preparation Methods, and Yields of **1–11**

no.	formula (molecular weight)		C (%)	H (%)	Hg (%) ^a	S (%)	starting component(g, mmol)	yield		mp (°C)	dec max. (°C)	
								(g)	(%)			
1	Hg(SCH ₃) ₂ (294.79)	calcd	8.15	2.05	68.05	21.76	a: Hg(N O ₃) ₂	1.97, 5.75	a: 1.66	a: 97.9	none	171
		found	8.18	1.98	-	20.9	d: Hg(SC ₂ H ₅) ₂	1.42, 4.40	d: 1.15	d: 88.6		175 ²⁰
							e: Hg	1.00, 4.99	e: 0.86	e: 58.5		
							f: HgCl ₂	1.14, 4.20	f: 1.18	f: 95.3		
2	Hg(SC ₂ H ₅) ₂ (322.842)	calcd	14.88	3.12	62.13	19.87	a: Hg(N O ₃) ₂	8.15, 23.8	a: 7.50	a: 97.7	79.6	189.4
		found	14.70	3.01	-	20.1	b: HgI ₂	1.01, 2.22	b: 0.51	b: 71.1	76 ⁵	
							c: Hg(SC ₅ H ₁₁) ₂	0.40, 0.98	c: 0.11	c: 34.7	72–73 ²⁰	
							d: Hg(SCH ₃) ₂	0.51, 1.73	d: 0.49	d: 87.7	77 ³⁵	
3	Hg(SC ₃ H ₇) ₂ (350.894)	calcd	20.54	4.02	57.17	18.28	e: Hg	0.83, 4.14	e: 0.47	e: 35.2		
		found	20.46	3.99	-	17.34	a: Hg(N O ₃) ₂	1.75, 5.11	a: 1.62	a: 90.4	71	170
							b: HgI ₂	1.04, 2.29	b: 0.62	b: 77.2	71–72 ⁵	
							d: Hg(SC ₈ H ₁₇) ₂	0.39, 0.79	d: 0.15	d: 53.8	67–69 ²⁰	
4	Hg(SC ₄ H ₉) ₂ (378.946)	calcd	25.35	4.79	52.94	16.92	e: Hg	0.57, 2.84	e: 0.17	e: 17.1	67 ³⁵	
		found	24.93	4.51	-	16.56	a: Hg(N O ₃) ₂	1.66, 4.85	a: 1.75	a: 95.3	89	196.1
							b: HgI ₂	1.09, 2.40	b: 0.60	b: 66.0	85–86 ⁵	
											81–83 ²⁰	
5	Hg(SC ₅ H ₁₁) ₂ (406.998)	calcd	29.51	5.45	49.29	15.76	a: Hg(N O ₃) ₂	1.72, 5.02	a: 2.04	a: 100	68.6	171.2
		found	29.00	5.34	-	15.67	b: HgI ₂	1.07, 2.36	b: 0.75	b: 78.3	74 ⁵	
							c: Hg(SCH ₃) ₂	0.30, 1.02	c: 0.39	c: 94.2	66 ³⁵	
							a: Hg(N O ₃) ₂	1.88, 5.49	a: 2.35	a: 98.4	61.5	169.9
6	Hg(SC ₆ H ₁₃) ₂ (435.05)	calcd	33.13	6.02	46.11	14.74	c: Hg(SC ₂ H ₅) ₂	0.44, 1.36	c: 0.35	c: 59.0	58 ³⁵	
		found	32.80	5.63	-	14.1	a: Hg(N O ₃) ₂	1.28, 3.74	a: 1.70	a: 98.3	81.1	197
							e: Hg	0.44, 2.19	e: 0.19	e: 18.7	76–77 ⁵	
											75 ³⁵	
7	Hg(SC ₇ H ₁₅) ₂ (463.102)	calcd	36.31	6.53	43.31	13.85	a: Hg(N O ₃) ₂	1.51, 4.41	a: 2.10	a: 97.0	74.8	234
		found	35.87	6.52	-	13.0	b: HgI ₂	3.62, 7.97	b: 3.56	b: 91.0	71 ³⁵	
							c: Hg(SC ₁₀ H ₂₁) ₂	0.43, 0.79	c: 0.28	c: 72.6		
							e: Hg	0.63, 3.14	e: 0.18	e: 11.7		
8	Hg(SC ₈ H ₁₇) ₂ (491.154)	calcd	39.12	6.98	40.84	13.06	a: Hg(N O ₃) ₂	1.24, 3.62	a: 1.72	a: 91.5		
		found	39.03	6.99	-	13.28	d: Hg(SCH ₃) ₂	0.45, 1.53	d: 0.55	d: 69.4		
							a: Hg(N O ₃) ₂	8.15, 23.8	a: 11.2	a: 86.0	69.1	242
							b: HgI ₂	1.14, 2.50	b: 1.34	b: 97.6		
9	Hg(SC ₉ H ₁₉) ₂ (519.206)	calcd	41.64	7.38	38.63	12.35	d: Hg(SC ₅ H ₁₁) ₂	0.24, 0.59	d: 0.26	d: 80.6		
		found	41.3	7.43	-	11.94	a: Hg(N O ₃) ₂	1.63, 4.76	a: 2.10	a: 73.2	96	276
							b: HgI ₂	1.27, 2.80	b: 1.61	b: 95.5		
10	Hg(SC ₁₀ H ₂₁) ₂ (547.258)	calcd	43.89	7.74	36.65	11.72						
		found	43.33	7.78	-	10.98						
11	Hg(SC ₁₂ H ₂₅) ₂ (603.362)	calcd	47.77	8.35	33.25	10.63						
		found	47.44	8.19	-	11.1						

^a not determined.

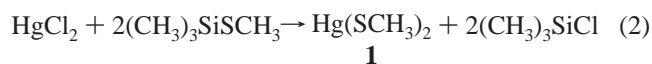
a series of compounds was prepared by common methods²³ to be used for analytical purposes and in further experiments as starting material. Furthermore, we extended the preparation to two new methods, one starting from mercury(II) iodide, alkanethiols, and trimethylamine and the other starting from mercury(II) chloride and trimethylsilyl methyl sulfide as the thiolate transferring reagent.

Ethanol solutions of 1 equiv of HgI₂ readily react at room temperature with 2 equiv of the corresponding *n*-alkanethiol to form voluminous colorless precipitates. By adding excess triethylamine as an auxiliary base, the precipitate becomes microcrystalline. The title compounds are obtained in high yield according to eq 1:



R = CH₃–C₅H₁₁ (**1–5**), C₈H₁₇ (**8**), C₁₀H₂₁ (**10**), C₁₂H₂₅ (**11**)

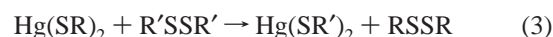
For the second method, HgCl₂ was suspended in dry benzene and reacted with trimethylsilyl methyl sulfide according to eq 2:



This method profits from the fact that the silyl sulfide is liquid at ambient temperature in contrast to CH₃SH boiling at approximately 6 °C. Second, the separation of the title com-

pound is very easy, because the corresponding trimethylchlorosilane can be evaporated together with the solvent.

Reactivity toward Organic Disulfides. Ligand exchange reactions of mercury thiolates are of particular interest with respect to biological systems. However, these reactions have been the subject of investigations concerning mainly methylmercury species.^{42,43} Bis(*n*-alkanethiolato)mercury(II) and organic disulfides easily exchange the thiolate functional groups already at ambient temperature in solvents and without solvent if the disulfide is employed in excess, according to eq 3:



R = R' = alkyl

GC and GC/MS investigations reveal the reaction to be an equilibrium proceeding together with an exchange reaction of the two diorganyl disulfide moieties resulting in the formation of the asymmetric disulfide RSSR' (eq 4):



R = R' = alkyl

Previously, the latter reaction could be demonstrated to be strongly accelerated by mercury or mercury thiolates.¹⁸

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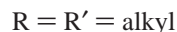
(43) Carty, A. J.; Carty, A. J.; Malone, S. F. *J. Inorg. Biochem.* **1983**, *19*, 133.

Table 2. IR and Raman Frequencies and Assignments of **1–5** in the Region of 800–50 cm⁻¹^a

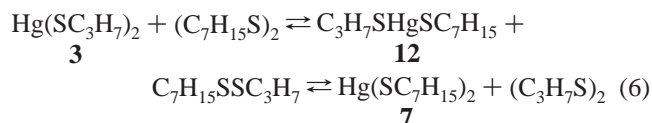
Hg(SCH ₃) ₂ (1)		Hg(SC ₂ H ₅) ₂ (2)		Hg(SC ₃ H ₇) ₂ (3)		Hg(SC ₄ H ₉) ₂ (4)		Hg(SC ₅ H ₁₁) ₂ (5)		assignment (proposed)
RE	IR	RE	IR	RE	IR	RE	IR	RE	IR	
		775 vvw	769 s		741 s	748 vw	781 m 744 m	749 vw	750 w	ρ(CH ₂)
695 m	694 s	657 s	671 vw 657 m	723 s	724 m	714 m	728 m, sh 720 vs	723 m	729 s 724 m, sh	ν(C–S)
						643 w	644 m			
						476 vw	477 vw	458 m	460 m	δ(C–C–C)
						430 vw	438 vw			δ(C–C–C)
						413 vw	408 w			
						351 w	346 m	367 w		δ(C–C–S)
				330 s	336 s–vs	324 w	322 m			
335 vw	341 s	415 vw, sh	407 vs	411 w	410 vs		250 vb		377 s	ν _{as} (Hg–S)
295 s	298 w	392 s	392 vw, sh	395 s	394 vw, sh	220 vs		350 s	349 vw	ν _s (Hg–S)
						264 m, sh				
175 m	199 w	244 s	268 s	203 s	225 m		210 m, sh	222 m	225 m	δ(C–S–Hg)
	156 w, sh	150 s	160 m		147 w					
	125 m, sh		140 m		129 m					
104 m	103 m, b	91 vs	90 s	115 s	111 m	126 s	120 m, sh	131 s		δ(S–Hg–S)
								113 m	110 s	
								91 w, sh		
81 sh	72 m		84 m, sh	89 vs	81 s	89 w	82 m	81 vs	88 s	τ(alkyl)
69 w	64 m	72 w, sh	64 vw	63 m	63 vw	62 vw, sh	66 vw	50 vw	69 m	τ(alkyl)

^a b = broad, s = strong, m = medium, w = weak, sh = shoulder, v = very; RE = Raman.

Interestingly, species of mercury compounds containing the two different thiolate groups, such as RSHgSR', could not be isolated. This result is in general agreement with that found for the reaction of Hg(SR)₂ compounds with organic thiols.¹⁸ However, in the presence of even catalytic amounts of diorganyl disulfide, an equilibrium according to eq 5



seems to be likely (cf. Figure 1). Our results are specifically based on investigations of the equilibria summarized in eqs 6 and 7:



If the starting components **3** and (C₇H₁₅S)₂ (eq 6) or **7** and (C₃H₇S)₂ (eq 7) are employed in stoichiometric amounts the total ion chromatograms (tics) of the two resulting reaction mixtures show after 48 h at ambient temperature a new, very weak signal at a retention time of approximately 45.5 min (inset in Figure 1a). Its mass spectrum indicates the in situ formation of compound **12**. Additional signals, two in both tics, are indicative of the corresponding symmetric disulfides and the asymmetric disulfide C₇H₁₅SSC₃H₇ (retention time = 27.4 min; Figure 1a).

After 216 h, the corresponding Hg(SR')₂ compounds can be clearly associated with another small signal appearing in the tics at either a retention time of 46.8 min (in the tic according to eq 6) or a retention time of 32.1 min (in the tic according to eq 7; Figure 1b). The corresponding compounds can be identified by their mass spectra as **7** (eq 6) and **3** (eq 7). Besides some additional signals of decomposition products, the tics of the reaction mixtures show the signals of all compounds as expected, except a defined signal for **12** (Figure 1b). Instead of

a sharp signal a very broad band (retention time interval = 40–46.5 min) appears.

Reaching the equilibrium state after approximately 360 h, the two signals in the tics corresponding to **3** and **7** interestingly almost disappear (indicating very low concentrations of the corresponding compounds) and a very broad signal (retention time interval ≈ 37–47 min) appears instead as exemplified for eq 7 (Figure 1c). This result suggests a complete equilibration of the two mercury thiolates.

All mass spectra obtained from the broad signals at different retention times are not consistent with a defined mercury compound, such as **12**. However, all these mass spectra suggest the presence of mercury thiolate species by their fragmentation signals.

Finally, it is possible to disturb the equilibrium state by addition of a great excess of one of the symmetric disulfides as shown for eq 7 (Figure 1d,e). The disulfide was added after 384 h. Tics were recorded after additional reaction times of 144 and 312 h, respectively. After 312 h, both the signal of the starting component **7** and the broad signal completely disappeared and **3** was formed instead (Figure 1e).

Furthermore, it is of great importance to notice that the title compounds obviously do not exchange the thiolate functional groups with each other (eq 5) under these particular conditions, however, in the absence of a diorganyl disulfide. These findings could be made plausible by accompanying GC experiments.

IR and Raman Spectra. Observed IR and Raman data of all compounds in the range 4000–800 cm⁻¹ are provided in Tables S1 and S2 (Supporting Information), those data in the range of 800–50 cm⁻¹ are listed in Tables 2 and 3. Examples of IR and Raman spectra in the frequency region of 850–50 cm⁻¹ are shown for **3**, **4**, **7**, and **8** (Figure 2a–d), respectively. Comparative data are given in Tables S3–S5 (Supporting Information).

IR and Raman spectra of bis(*n*-alkanethiolato)mercury(II) compounds and of related Hg(SR)₂ moieties in the solid state are scarcely discussed.^{18,21,22a,28,39,41,44–47} In some cases discussions have been even contradictory to each other.^{21,22a} Moreover, some data²¹ are in contrast to the results of X-ray structural analysis,^{13–16} whereas other data compare very well.^{22a}

Table 3. IR and Raman Frequencies and Assignments of **6–11** in the Region of 800–50 cm⁻¹ ^a

Hg(SC ₆ H ₁₃) ₂ (6)		Hg(SC ₇ H ₁₅) ₂ (7)		Hg(SC ₈ H ₁₇) ₂ (8)		Hg(SC ₉ H ₁₉) ₂ (9)		Hg(SC ₁₀ H ₂₁) ₂ (10)		Hg(SC ₁₂ H ₂₅) ₂ (11)		assignment (proposed)
RE	IR	RE	IR	RE	IR	RE	IR	RE	IR	RE	IR	
	781 m				781 vw	760 vw	760 vw		783 m		752 m	
	738 m, sh	755 vvw	757 m		740 m		732 m, sh	747 vw	728 s, sh		725 m, sh	$\rho(\text{CH}_2)$
727 s	728 vs	726 s	726 vs	724 vs	719 vs	724 s	718 vs	724 s	717 vs	725 s	717 vs	$\nu(\text{C-S})$
					713 w, sh	714 w, sh		716 w, sh				
456 m	456 m	479 vw	479 m	490 vw	489 vw	489 w	489 vw	502 vw	500 vvw	502 vw	500 vw	$\delta(\text{C-C-C})$
435 m	438 m	440 m	442 m	449 vw	448 vw	478 vw	480 vw	480 vw	480 vw			$\delta(\text{C-C-C})$
				403 m	402 vs			428 vw	425 m	427 m	426 m	
				380 m	378 vw	395 m		378 vw	378 s	372 vw	373 s	$\delta(\text{C-C-S})$
						360 vw		366 m	366 vw, sh			
365 vw	365 vs		389 vs	347 vw, sh	348 vs		396 vs		355 m	345 w, sh	347 m	$\nu_{\text{as}}(\text{Hg-S})$
			345 vvw				342 s	343 vs				
340 vs	339 vvw	375 s		329 s			381 m	381 vw	335 s		332 s	$\nu_{\text{s}}(\text{Hg-S})$
305 vvw	279 w	303 s	316 m	288 m	289 vw		308 s	308 vw	308 vw	336 m	309 vvw	309 w
282 w							231 m	230 w	270 m	269 w	282 vw	283 vw
192 m	201 m	253 m	253 m	242 m	241 w	189 m	191 m	224 w	222 w	223 vw	222 vw	$\delta(\text{C-S-Hg})$
				210 w	210 w	243 vvw		203 vvw		206 w		
										185 vw	183 vw	
169 vvw		159 m	164 m	159 vvw	162 w	154 w	152 vw	164 m	168 w	168 vw		
139 vw	143 w	133 vw	132 m	139 m			137 w	131 w	131 w	133 m		
			117 w				120 m	118 vw	105 m, sh			
101 vs	102 s	100 vs	95 vs	114 m	113 m	105 m	107 m	97 vs	97 m	109 m	110 m	$\delta(\text{S-Hg-S})$
	90 m			100 vw, sh	95 w		90 m			90 vs	90 m	
		85 w, sh	85 m	87 vs	87 m	85 vs	82 m	86 w, sh	84 m			$\tau(\text{alkyl})$
65 m	73 w	75 vw, sh	70 vw	64 vw, sh	77 w, sh	64 w, sh	70 w, sh	75 m	74 m	63 vw	75 m	$\tau(\text{alkyl})$

^a b = broad, s = strong, m = medium, w = weak, sh = shoulder, v = very; RE = Raman.

The frequency window of the Hg–S-stretching vibrations is approximately 400–180 cm⁻¹. The IR active $\nu_{\text{as}}(\text{Hg-S})$ stretching is generally located at higher frequencies compared to the corresponding Raman active $\nu_{\text{s}}(\text{Hg-S})$ stretching modes. The difference between the two frequencies is approximately an order of magnitude of 15–40 cm⁻¹ in the case of linear and tetrahedral coordination of mercury. The position of Hg–S stretching modes strongly depends on the coordination number of mercury, where only atoms which are strongly bonded to mercury (average bond length below ca. 2.8 Å) are of influence on the relevant vibrational modes.^{22,39} Increasing coordination from two to four corresponds with a decrease and with splittings of Hg–S frequencies and modes, respectively. This finding is nowadays generally accepted. The coordination number of mercury correlates with the Hg–S frequencies not only for the discussed compounds, but also for related mercury thiolate compounds, as is discussed and well-documented for a series of RSHgX compounds.^{22b}

Generally, homoleptic thiolate complexes of mercury show a considerable variation in their coordination geometry,^{13–18,27,29,39,47–55} but the factors determining these geometries are not yet clear.⁵⁶ X-ray structural analysis showed most of the hitherto investigated bis(*n*-alkanethiolato)mercury(II)

compounds to exhibit an almost linear S–Hg–S skeleton with a primary coordination of two for mercury.^{13–16,18} Accordingly, two Hg–S stretching modes can be expected in the vibrational spectra. These IR active $\nu_{\text{as}}(\text{Hg-S})$ and Raman active $\nu_{\text{s}}(\text{Hg-S})$ stretchings can be assigned without any doubt for **1**, **2**, **5**, **6**, and **8** (Figure 2d), being the only acceptable pairs of modes with satisfying intensity in the relevant frequency region. The presence of weak forbidden IR and Raman counterparts for the majority of these bands support the assignment. For **10** and **11** no particular vibrational coupling with $\nu(\text{Hg-S})$ will be expected in comparison to **8**. Therefore, suitable modes at 335 and 355 cm⁻¹ for **10**, as well as 332 and 347 cm⁻¹ for **11**, are assigned to the $\nu(\text{Hg-S})$ stretchings (Table 3). Compound **4** (Figure 2b) does not cause $\nu(\text{Hg-S})$ stretchings comparable to the other title compounds because of its sulfur-bridged crystal structure, which varies from the other compounds, thus exhibiting the coordination number four for mercury.¹⁷ For the remaining compounds **3** (Figure 2a), **7** (Figure 2c), and **9**, two pairs of bands can alternatively be considered for the $\nu(\text{Hg-S})$ stretching modes (Tables 2 and 3). We ascribe the pairs of vibrations situated at the higher frequencies to the $\nu(\text{Hg-S})$ stretchings of compounds **3**, **7**, and **9**, respectively. A suitable explanation for this assignment can be given with the comparable behavior of the $\nu(\text{S-S})$ stretchings of di-*n*-alkyl disulfides.⁵⁷ The derivatives with odd-numbered carbon chains exhibit these stretching modes at higher frequencies compared to those derivatives with even-numbered carbon chains. This behavior can be made plausible by the different packing of even and odd numbered alkyl groups, as suggested for long-chained paraffins.⁵⁸ In the special case of compound **3**, the proposed assignment can be additionally supported by taking into consideration that forbidden IR and Raman counterparts are showing up as weak bands.

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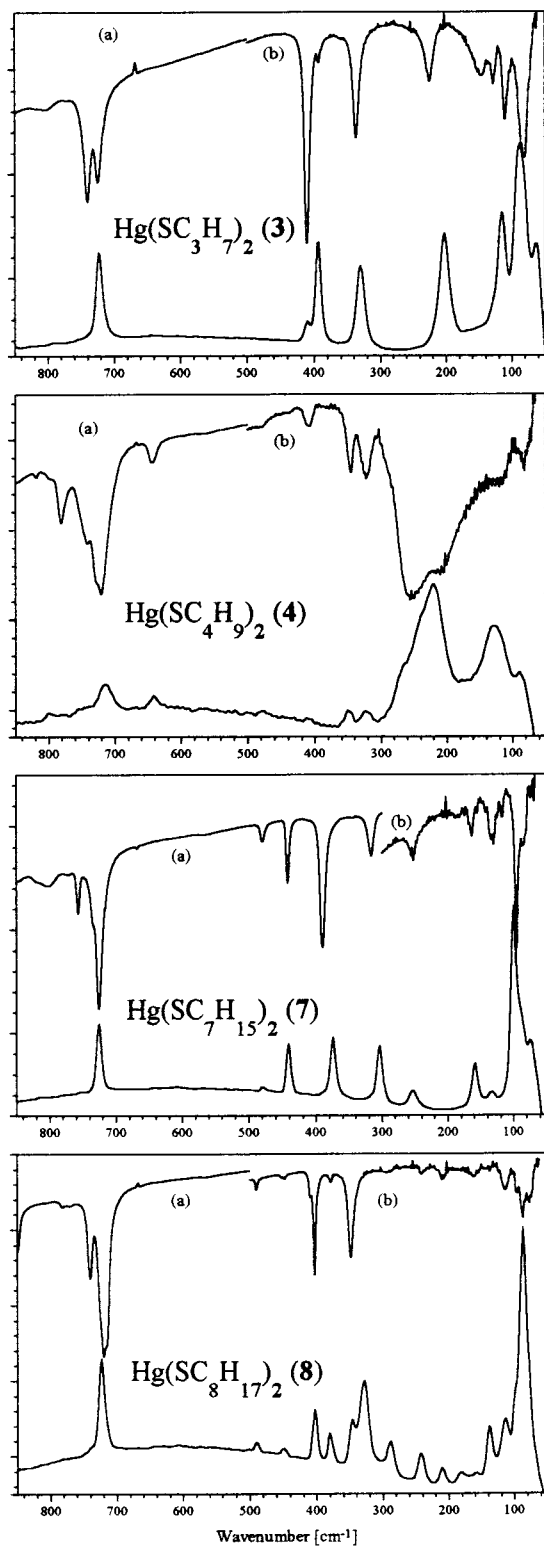


Figure 2. Infrared (upper) and FT-Raman (lower) spectra of **3** (2a), **4** (2b), **7** (2c), and **8** (2d) at room temperature in the region 850–50 cm^{-1} : (a) CsI, pellet and (b) PE Nujol.

On the other hand, the bands at 330 and 336 cm^{-1} have to be kept in mind for these modes, too, as they are reasonably positioned in the relevant region. Comparing the compounds with an even-numbered alkyl chain, as well as those compounds with an odd-numbered alkyl chain, with each other, one can observe a slight decrease of the $\nu(\text{Hg}-\text{S})$ stretchings going along with an increasing chain length of the ligand for those compounds with an even-numbered alkyl chain (however, with

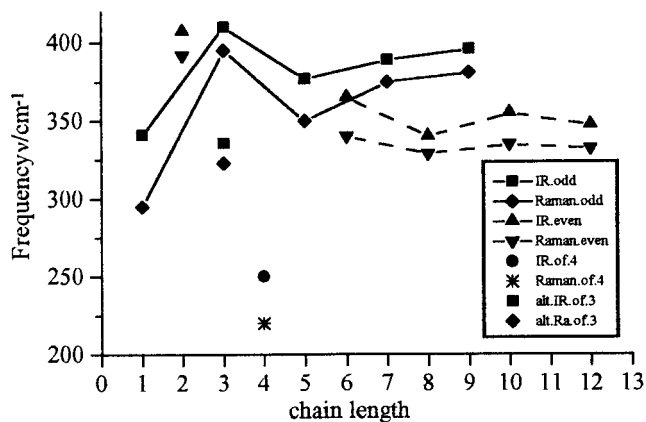


Figure 3. Correlation of $\nu_s(\text{Hg}-\text{S})$ and $\nu_{as}(\text{Hg}-\text{S})$ frequencies to the chain length of the alkyl substituents of the title compounds.

the exception of **4**); on the other hand, for those compounds with an odd-numbered alkyl chain, the $\nu(\text{Hg}-\text{S})$ stretchings are slightly increasing with an increasing alkyl chain number (however, **3** is an exception if the higher modes at 395 and 403 cm^{-1} are considered). These results can clearly be seen in Figure 3. Finally, the position of the discussed $\nu(\text{Hg}-\text{S})$ stretchings for **1–3** and **5–11** at high frequencies is indicative of a coordination of two at the central mercury.^{28,56}

Other modes of significance are the $\delta(\text{S}-\text{Hg}-\text{S})$ bendings. Generally, the difference between the IR-active $\delta_{as}(\text{S}-\text{Hg}-\text{S})$ and the Raman-active $\delta_s(\text{S}-\text{Hg}-\text{S})$ mode can be expected to be small. It is unfortunate, but especially in the case of these compounds, only for **1** are IR-active bendings discussed and assigned at 126 and 95 cm^{-1} .⁴⁴ For some related complexes $\delta(\text{S}-\text{Hg}-\text{S})$ bendings are given in the region between approximately 170 and 90 cm^{-1} .^{39,59} With the exception of **4**, all title compounds show medium–strong bands within the frequency window reaching from 115 to 90 cm^{-1} , which can be attributed to these $\delta(\text{S}-\text{Hg}-\text{S})$ bendings (Tables 2 and 3). Skeletal bending modes $\delta(\text{C}-\text{S}-\text{Hg})$ are expected to occur below approximately 250 cm^{-1} , however, at significantly higher frequencies than the $\delta(\text{S}-\text{Hg}-\text{S})$ bendings. For **1** and **2** Raman-active modes have been suggested in the region from 175 to 150 cm^{-1} .^{21,44} For the corresponding cyclohexanethiolato derivative, this mode as well as its IR-active counterpart are given at 159 cm^{-1} .³⁹ The IR-active counterpart for **1** has been assigned to 198 cm^{-1} .⁴⁴ In our opinion, a detailed assignment of these modes still seems to be highly speculative. Therefore, our assignments presented in Tables 2 and 3 have to be seen as only tentative. In some of the previous studies other modes of interest, such as $\nu(\text{C}-\text{S})$, $\delta(\text{C}-\text{C}-\text{C})$, and $\delta(\text{C}-\text{C}-\text{S})$, as well as rockings, such as $\rho(\text{CH}_2)$, are reported.^{21,22a,39,44,45,60,61} These modes occur in the region from approximately 800 to 350 cm^{-1} . Thus, it has to be taken into account that they may overlap each other, and in addition, some of these modes may overlap the $\nu(\text{Hg}-\text{S})$ stretchings, too. Appropriate assignments are given for all compounds in Tables 2 and 3 without further discussion.

Bands observed in the region from 750 to 650 cm^{-1} can be assigned definitely to CH_2 rocking and $\text{C}-\text{S}$ stretching vibrations (Tables 2 and 3).^{21,44,57} Especially in case of longer chain substituents, very low-frequency bands may be caused by so-called longitudinal accordion motions (LAM modes) as for

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Table 4. GC/MS Data, Mass Spectra, and the Main Fragmentation Pattern of **1–11** Together with Their Decomposition Products, the Corresponding Di-*n*-alkyl Disulfides (C_{*n*}H_{2*n*+1})₂S₂ for *n* = 1–10, 12

no.	formula	MW	retention (min)	M ⁺ ^a	fragmentation (main peaks)									
					CH ₂ SHgSH ^a	CH ₂ SHgSR ^a	RSHgSH ^a	RSHg ^a	Hg(SH) ₂ ^a	HgS ^a	Hg ^a	RSSR ^b	RSSH	RS
1	(CH ₃ S) ₂	94.20	3.4	-	-	-	-	-	-	-	-	94	79 ^c	47
	Hg(SCH ₃) ₂	294.79	25.7	296	281	285	282	249	268	234	202	94	79 ^c	47
2	(C ₂ H ₅ S) ₂	122.252	9.7	-	-	-	-	-	-	-	-	122	94	66 ^d
	Hg(SC ₂ H ₅) ₂	322.842	28.7	324	281	309	296	263	268	234	202	122	94	66 ^d
3	(C ₃ H ₇ S) ₂	150.304	16.1	-	-	-	-	-	-	-	-	150	108	66 ^d
	Hg(SC ₃ H ₇) ₂	350.894	32.1	352	281	323	310	277	268	234	202	150	108	66 ^d
4	(C ₄ H ₉ S) ₂	178.356	22.5	-	-	-	-	-	-	-	-	178	122	
	Hg(SC ₄ H ₉) ₂	378.946	36.4	380	281	337	324	291	268	234	202	178	122	
5	(C ₅ H ₁₁ S) ₂	206.408	27.3	-	-	-	-	-	-	-	-	206	136	103
	Hg(SC ₅ H ₁₁) ₂ ¹⁸	406.998	40.4	408	281	351	338	305	268	234	202	206	136	103
6	(C ₆ H ₁₃ S) ₂	234.46	31.8	-	-	-	-	-	-	-	-	234	150	117
	Hg(SC ₆ H ₁₃) ₂	435.05	43.7	436	281	365	352	319	268	234	202	234	150	117
7	(C ₇ H ₁₅ S) ₂	262.512	36.1	-	-	-	-	-	-	-	-	262	164	131
	Hg(SC ₇ H ₁₅) ₂	463.102	46.8	464	281	379	366	333	268	234	202	262	164	131
8	(C ₈ H ₁₇ S) ₂	290.564	40.0	-	-	-	-	-	-	-	-	290	178	145
	Hg(SC ₈ H ₁₇) ₂	491.154	49.9	492	281	393	380	347	268	234	202	290	178	145
9	(C ₉ H ₁₉ S) ₂	318.616	43.5	-	-	-	-	-	-	-	-	318	192	159
	Hg(SC ₉ H ₁₉) ₂	519.206	- ^e	-	-	-	-	-	-	-	-	-	-	-
10	(C ₁₀ H ₂₁ S) ₂	346.668	46.8	-	-	-	-	-	-	-	-	346	206	173
	Hg(SC ₁₀ H ₂₁) ₂	547.258	- ^e	-	-	-	-	-	-	-	-	-	-	-
11	(C ₁₂ H ₂₅ S) ₂	402.772	52.6	-	-	-	-	-	-	-	-	402	234	201
	Hg(SC ₁₂ H ₂₅) ₂	603.362	- ^e	-	-	-	-	-	-	-	-	-	-	-

^a Main peak of the isotope pattern of mercury. ^b 100% signal. ^c RSS. ^d HSSH. ^e Decomposition of the mercury compound on the column.

example discussed for fatty acids,^{62a} and other suitable compounds.^{62b}

With respect to the already published data for **1**,^{21,22a,44} **2**,^{21,22a} **3**,²¹ and **4**,^{21,41} the following conclusions can be drawn. For **1** (Table S3) a reasonable assignment supported by a vibrational analysis is already presented.⁴⁴ Our frequency values are in accordance with these data; moreover, we strictly follow the given assignments. Especially for the $\nu(\text{Hg}-\text{S})$ stretchings, additional data are available and are all in accordance with both the above-mentioned values and the vibrational analysis.^{21,22a} Our spectral data of **2** (Table S4) harmonize well with those already presented.^{22a} Moreover, in accordance with the given frequencies, we assign the $\nu(\text{Hg}-\text{S})$ stretchings to $\nu_{\text{as}} = 407 \text{ cm}^{-1}$ and $\nu_{\text{s}} = 392 \text{ cm}^{-1}$, respectively. However, these assignments are contradictory to other data,²¹ where the assigned frequencies for the $\nu(\text{Hg}-\text{S})$ stretchings are obviously far too low, considering that in **2** mercury has a coordination number of two. In addition, the published spectral data are obviously incomplete for the lower frequency region.^{21,22a} In our opinion, the same discussion can be easily transferred to **3**. Assignments of the modes of this compound already exist.²¹ However, once more, the frequencies of the $\nu(\text{Hg}-\text{S})$ stretchings are assigned far too low (Table S4).²¹ Moreover, the assignment is in contrast to the crystal structure determination discussed for **3**, presenting the coordination number two for mercury.¹³ Therefore, we preferably suggest the bands at 395 and 402 cm^{-1} to these stretchings. However, keep in mind that it also remains possible to assign the frequencies at 330 and 336 cm^{-1} to these stretchings, especially as they would almost perfectly fit in the plot for the compounds with an odd-numbered alkyl chain (Figure 3).

Finally and as already mentioned, for **4** surprisingly a four-coordinated central mercury could be clearly established by X-ray structural investigations.^{13,17} Accordingly, $\nu(\text{Hg}-\text{S})$ stretchings are situated at significantly lower frequencies in the corresponding frequency window. That is the reason the spectra of this particular compound cannot be compared with those of all other compounds investigated (cf. Figure 3 and Table S5). Remarkably and in contrast to all other title compounds, the

spectra of **4** reveal very broad IR as well as Raman bands at 250 and 220 cm^{-1} , respectively (Figure 2b). In this case, as for **1**, we support the data already presented.²¹ In addition, the IR data are in accordance with those data given elsewhere, however, without presenting defined assignments.⁴¹

Identification of Hg(SR)₂ by Means of Gas Chromatography–Mass Spectrometry (GC/MS). GC/MS investigations clearly reveal the title compounds to be monomeric in the gas phase. As expected, they easily undergo decomposition at elevated temperatures. The main decomposition products are mercury and the corresponding dialkyl disulfides as is revealed in the obtained tics. For those mercury compounds with a lower molecular weight (up to **8**), the decomposition products can be identified in both the tics and the mass spectra of the parent compounds, in the latter as the main fragmentation products. Moreover, the signal intensities of the bis(*n*-alkanethiolato)-mercury(II) compounds in the tics are significantly decreasing with increasing molecular weight of the mercury compound, whereas the corresponding signals of the decomposition products are increasing. This general finding is due to the enhanced decomposition of these compounds, caused by their progressively longer retention times on the GC column. Compounds **9–11** already decompose on the GC column. This is the reason why only the corresponding decomposition products (mainly the dialkyl disulfides and in a minor amount the dialkyl sulfides) can be detected for these compounds in the tics of GC/MS recordings; however, no signal of the parent compound is seen. The results are in agreement with the thermochemical behavior of the title compounds.^{18,33,38,63–67} The fragmentation of all mercury compounds is given in Table 4.

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Conclusion

$\text{Hg}(\text{SC}_n\text{H}_{2n+1})_2$ for $n = 1-10, 12$ (compounds **1-11**, respectively) have been prepared from HgI_2 and *n*-alkanethiol using $\text{N}(\text{C}_2\text{H}_5)_3$ as an auxiliary base. An elegant alternative route is given with the exchange reaction of mercury(II) chloride with trimethylsilyl organyl sulfides. IR and Raman data indicate the mercury compounds to be monomeric with an almost linear S—Hg—S skeleton in the solid state with the exception of **4**, the spectra of which exhibit the compound to be four coordinated at the central mercury. The title compounds easily exchange the thiolate functional groups with corresponding diorganyl disulfides already at ambient temperature, however in a complicated exchange process including an equilibration of the symmetric diorganyl disulfides with their asymmetric counterpart. Interestingly, asymmetric $\text{R}'\text{SHgSR}$ moieties cannot be practically isolated. However, GC/MS investigations show that there is at least evidence for these compounds in the in situ reaction mixtures, indicated by very weak signals in the

tics, the corresponding mass spectra of which show a molecular ion $\text{R}'\text{SHgSR}^+$ with the mercury isotope pattern.

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Supporting Information Available: Complete lists of IR and Raman data for all compounds (Tables S1 and S2). Comparison of literature data of the IR and Raman spectra of compounds **1-4** (Tables S3-S5). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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