Formation of Extended 1D and 2D Coordination Polymers in Tetrathioether Complexes of Mercury(II) and Copper(I): Crystal Structures of [{{Ge(CH₂SPh)₄}HgBr₂}_n] and [{{Ge(CH₂SPh)₄}(Cu₂l₂}_n]

Harmel N. Peindy,^[a] Fabrice Guyon,^[a] Abderrahim Khatyr,^[a] Michael Knorr,^{*[a]} Viktoria H. Gessner,^[b] and Carsten Strohmann^{*[b]}

Dedicated to Professor Michael Veith on the Occasion of His 65th Birthday

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Abstract. A one-dimensional (1D) coordination polymer of stoichiometry [{ $Ge(CH_2SPh)_4$ }HgBr₂}_n] (2b) has been prepared by treatment of HgBr₂ with the functionalized germane Ge(CH₂SPh)₄ (1b), which is acting as a tetradentate thioether ligands. The extended structure results from weak intermolecular Hg-S interactions linking the monomeric {Ge(CH₂SPh)₄}HgBr₂ units, as established using single-crystal X-ray diffraction. The effective coordination around the mercury atoms is best described as distorted octahedral. Upon reaction of CuI with 1b in a 2:1 metal-to-ligand ratio, the

Introduction

Bi- and polydentate thioethers represent an emerging class of flexible ligands for various applications such as molecular electronics, catalysis, stabilization of colloids, preparation of self-assembled monolayers on gold surfaces, and the elaboration of luminescent compounds [1-4]. Furthermore, they are particularly interesting since they can act as flexible building blocks (tectons) with the ability to generate diverse metal organic coordination networks in autoassembly processes [5]. In the past, *Siemeling* [3b], *Rabinovich* [11–14] and our group [6–10] have reported on the synthesis of silicon-based bidentate and tridentate thioethers $R_{4-n}Si(CH_2SR)_n$ (n = 2, 3; R = Me, Ph) and characterized a wide variety of transition metal complexes in which they act as either terminal or bridging ligands. More recently, we have demonstrated in a collaborative

* Prof. Dr. M. Knorr

- E-Mail: michael.knorr@univ-fcomte.fr * Prof. Dr. C. Strohmann
- E-Mail: carsten.strohmann@uni-dortmund.de [a] Institut UTINAM UMR CNRS 6213

Université de Franche-Conté 16, Route de Gray 25030 Besançon, France

[b] Technische Universität Dortmund Anorganische Chemie Otto-Hahn Strasse 6 44227 Dortmund, Germany novel metal-organic polymer $[\{\{Ge(CH_2SPh)_4\}(Cu_2I_2)\}_n]$ (3), which incorporates rhombic dinuclear $Cu(\mu-I)_2Cu$ units within its 2D sheet-like network, was obtained. The luminescence properties of **1b** and **3** have been investigated both in solution and in the solid state. Upon treatment of **1b** with $[\{Re(\mu-Br)(CO)_3(THF)\}_2]$ the mononuclear compound *fac*-[ReBr(CO)_3{Ge(CH_2SPh)_4}] (4) is formed. In this chelate complex, two CH_2SPh arms are ligated on Re^I, the remaining two CH_2SPh arms are dangling.

work that tetrathioether ligands of type $Si(CH_2SR)_4$ (R = Me, Ph) may be used as assembling ligands to construct mono-dimensional coordination polymers of type [{ $Si(CH_2SR)_4$ }HgBr₂]_n] upon reaction with HgBr₂ [15a, b]. The heavier tin congener Sn(CH₂SPh)₄ (1c) has been described 35 years ago [16], and the derivative Sn(CH₂SMe)₄ has quite recently been employed as precursor for the preparation of the 1D coordination polymer [{ $Sn(CH_2SMe)_4$ }(ZnCl₂)₂]_n][17].

Continuing our studies on multidentate thioethers, we now set out to evaluate and compare the coordinative properties of the tetrathioether ligand $Ge(CH_2SPh)_4$ (**1b**) with those of its silicon analogue Si(CH_2SPh)_4 (**1a**) [7, 15c]. The synthesis and molecular structure of **1c** has recently been described by *Strohmann* et al. [18]. We report herein on the preparation and crystallographic characterization of metal-organic 1D and 2D networks of Hg^{II} and Cu^I incorporating this germanium-based ligand system and present their luminescence properties. For comparison, a mononuclear compound *fac*-[ReBr(CO)₃{Ge(CH₂SPh)₄}] has been prepared.

Experimental Section

MeCN was dried with molecular sieves before use, toluene with sodium and dichloromethane with P_4O_{10} . IR spectra have been recorded with a Nicolet Nexus 470 spectrometer, UV/Vis spectra with a Uvikon-XL spectrometer. The liquid and solid-state emission



spectra were recorded with a Jobin-Yvon Fluorolog-3 spectrometer using a cylindrical 0.5 cm diameter quartz capillary with a scan speed of 1 nm \cdot s⁻¹. Emission intensity are normalized for comparison. Elemental C, H analyses were performed with a Leco Elemental Analyser CHN 900. The ¹H-NMR spectra were recorded at 300.13 MHz with a Bruker Avance 300 instrument. [{Re(µ-Br) (CO)₃(THF)}₂] was prepared according to ref [19].

Preparation of 1D Polymer $[{{Ge(CH_2SPh)_4}HgBr_2}_n]$ (2b)

To a suspension of HgBr₂ (360.5 mg, 1 mmol) in toluene (10 mL) was added **1b** (565 mg, 1 mmol). The solution was heated to reflux for 5 min and the stirred at 25 °C for 24 h. Layering the clear solution with hexane afforded colorless crystals, suitable for X-ray diffraction. Yield: 0.796 g, 81 %. Anal. $C_{28}H_{28}Br_2GeHgS_4(925.82)$: C, 36.32; H 3.05; found: C, 36.81; H 3.5 %. ¹H NMR (CDCl₃): δ = 2.86 (s, 8 H, SiCH₂), 7.15–7.42 (m, 20 H, C₆H₅).

Preparation of 2D Polymer [$\{\{Ge(CH_2SPh)_4\}(Cu_2I_2)\}_n$] (3)

To a suspension of CuI (382 mg, 2.0 mmol) in MeCN (10 mL) was added **1b** (565 mg, 1.0 mmol). The mixture was refluxed for 5 min, then the solution was allowed to reach room temperature. After one day, colourless crystals of **3b** were formed. Yield 0.681 g, 72 %. $C_{28}H_{28}Cu_2GeI_2S_4$ (946.21): calcd. C 35.54, H 2.99; found C 35.89, H 2.55.

Preparation of $[ReBr(CO)_3]_2\{(PhSCH_2)_4Ge)\}(4)$

[{Re(μ -Br)(CO)₃(THF)}₂] (211 mg, 0.25 mmol) was dissolved in 7 mL of dichloromethane and **1b** (286 mg, 0.51 mmol) was added to the solution. The reaction mixture was stirred at room temperature for 1h, then reduced to ca. 5 mL and layered with heptane. Yield 0.347 g, 76 %. Anal. C₃₁H₂₈BrGeO₃ReS₄ (915.56): C, 40.67; H, 3.08; S 14.01; found: C, 40.41; H, 3.23; S, 13.96. – IR(CH₂Cl₂): v(CO) = 2039s, 1953s, 1913s cm⁻¹. ¹H NMR: δ = 2.70 (s, 4H), 2.74 (d, H_A, 2H, ²J_{HAHB} = 10.1 Hz), 3.79 (d, H_B, 2H, ²J_{HAHB} = 10.1 Hz).

X-ray Structure Determinations

Suitable crystals of 2b and 3 were covered with inert oil (perfluoropoly-alkylether) and used for X-ray crystal structure determinations. X-ray diffraction data of all structures were recorded at 193(2) K (compound 2b) and 173(2) K (compound 3) with the Stoe-IPDS diffractometer. Graphite monochromated Mo-K_a radiation ($\lambda = 0.71073$ Å) was used. The crystal structure was solved with direct methods and refined against F^2 with the full-matrix least-squares method (SHELXS-90, SHELXL-97) [20]. An numerical absorption correction was employed using the FACEIT-program in IPDS (Stoe & Cie, 1999). For each structure, the nonhydrogen atoms were refined anisotropically. All of the hydrogen atoms were placed in geometrically calculated positions and each was assigned a fixed isotropic displacement parameter based on a riding-model. Refinement of the structures was carried out by fullmatrix least-squares methods based on F_o^2 using SHELXL-97. Information concerning the data collection and processing, crystallographic parameters, and details on structure solution and refinement are given in Table 3. Selected bond lengths and angles are shown in Table 1 and Table 2, respectively.

Crystallographic data for the structures (**2b**: CCDC-698030, **3**: CCDC-698029) has been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2, 1EZ, UK (Fax: int.code+44-1223-336-033; E-Mail for inquiry: fileserv@ccdc.cam.ac.uk; E-Mail for deposition: deposit@ccdc.cam.ac.uk).

Results and Discussion

Synthesis and Structural Characterization of 1D Metallopolymer [$\{\{Ge(CH_2SPh)_4\}HgBr_2\}_n$] (2b)

The polymeric complex $[{{Ge(CH_2SPh)_4}HgBr_2}_n]$ (2b) was prepared by treatment of mercury(II) bromide with an equimolar amount of ligand 1b (Scheme 1) in hot toluene and isolated as white, air-stable solid in 58 % yield. It is moderately soluble in chlorinated hydrocarbons and was characterized by a combination of analytical and spectroscopic techniques. The ¹H-NMR spectrum in CDCl₃ exhibits a singlet resonance for the methylene protons at δ = 2.86, which is slightly downfield-shifted relative to the free ligand ($\delta = 2.60$) in the same solvent. The presence of only one broadened signal for the four methylene groups even at temperatures down to 243 K indicates a highly flexible (i.e., labile) system in solution. It is noteworthy that according to studies by Goodall, no mercury-thioether adduct could be obtained by treatment of HgBr₂ with the tetrathioether ligand C(CH₂SPh)₄ [21].



Scheme 1. $E(CH_2SPh)_4$ as building block for the assembly of 1D and 2D polymers.

The molecular structure of **2b**, which crystallizes in the triclinic crystal system, space group $P\overline{1}$, was determined by single-crystal X-ray diffraction analysis. The polymeric crystal structure is comparable to the silicon analogue, $[{Si(CH_2SPh)_4}HgBr_2]_n$ (**2a**) [15a, 22]. The repeating mo-



lecular motif, which is depicted in Figure 1, consists of a fairly linear $HgBr_2$ unit, which is coordinated by the sulfur atoms of the two PhSCH₂-arms of ligand **1b**. The resulting Hg-S-C-Ge-C-S six-membered ring adopts a rather twisted conformation.



Figure 1. Thermal ellipsoid plot of the molecular motif of $[\{ Ge(CH_2SPh)_4\} HgBr_2\}_n]$ (2b).

The Hg-S distances in the central motif of 2.988(3) and 3.005(25) Å are quite long, but similar to those [2.989(2) and 2.994(2) Å] found in the silicon derivative 2a [15a]. Significantly shorter bond lengths than those of 2a, b have been reported for the dinuclear compound $[(1,4,7,10,13,16,19,22-\text{octathiahiacyclotetracosane})(\text{HgBr}_2)_2].$ In this thiacrown-ether complex, the mercury atom is ligated through two short Hg-S bonds [2.581(4) and 2.835(4) Å], whereas an additional third weak intermolecular Hg-S bond of 3.110(4) Å results in a distorted trigonal bipyramidal arrangement to the metal atoms [23]. In the macrocyclic dinuclear complex [(1,4,7,10,13,16-hexathiacyclooctadecane)(HgBr₂)₂] the average bond length between the thia donors and the two HgII atoms amounts to 2.772(5) A [24]. Consequently, no correlation between the nature of a given thioether ligand and the Hg-S bond length to a HgBr₂ moiety is evident. Even in the case of an identical $-CH_2-S-Ph$ functionality, the Hg-S bond lengths are quite variable. For instance, in the 2D-coordination polymer [{PhS(CH₂)₄SPh)₄}Hg₂Br₄}_n], the Hg-S bond lengths amount to 2.499(3) Å [25], whereas in the 3D coordination polymer [{PhS(CH₂)₂SPh)₄}Hg₂Br₄}_n] significantly longer bond length of 2.8963(17) Å have been observed [26, 27].

In the crystal, $[{Ge(CH_2SPh)_4}HgBr_2]_n]$ (2b) forms an extended polymeric structure due to two additional weak intermolecular thioether interactions of 3.230(3) and 3.237(3) Å. This arrangement results in a distorted octahedral environment of the mercury atoms with a total of four Hg-S and two Hg-Br bonds. The corresponding cisangles in 2b span the range of 78-98°. Corresponding with this pseudo-octahedral arrangement, the deviation from linearity of the Br-Hg-Br angle [169.882(17)°] is not very pronounced. The Hg-Br bond lengths observed in 2b [2.4521(7) and 2.4540(6) Å] correspond to those in 2a [2.4564(10) and 2.4571(10) Å]. Similar values were also encountered in $[{PhS(CH_2)_4SPh}_4]Hg_2Br_4]_n$ with 2.4404(8) and 2.4592(7) Å [25]. Interestingly, in the resulting infinite 1D ribbon of $[{Ge(CH_2SPh)_4}HgBr_2]_n]$ (2b), all phenyl substituents adopt an almost parallel syn-orientation with a cutting angle of the normals of the two best planes of 2.31(1) and 1.65(1)° (Figure 2, Table 1). However, the shortest distances between the planes amount to ~ 3.66 Å, thus

Table 1. Selected bond length /Å and angles /° of compound 2b.

Hg-S(1)	2.988(3)	Br(1)-Hg-S(4)	94.54(4)
Hg-S(2)	3.005(2)	Br(2)-Hg-S(1)	92.13(6)
Hg-S(3)	3.237(3)	Br(2)-Hg-S(2)	95.52(5)
Hg-S(4)	3.230(3)	Br(2)-Hg-S(3)	93.99(4)
Hg-Br(1)	2.456(1)	Br(2)-Hg-S(4)	77.93(4)
Hg-Br(2)	2.457(1)	S(1)-Hg-S(2)	84.46(6)
		S(1)-Hg-S(3)	98.18(4),
Br(1)-Hg-Br(2)	169.88(2)	S(1)-Hg-S(4)	169.96(5)
Br(1)-Hg-S(1)	95.15(6)	S(2) - Hg - S(3)'	170.03(3)
Br(1)-Hg-S(2)	92.17(5)	S(2)-Hg-S(4)	97.81(4),
Br(1)-Hg-S(3)	78.05(4)	S(3)' - Hg - S(4)'	81.26(5)



Figure 2. View of the crystal structure of $[\{\{Ge(CH_2SPh)_4\}HgBr_2\}_n]$ (2b) along the *a*-axis.

excluding relevant $\pi - \pi$ -stacking interactions. Consequently, the *syn*-orientation can be attributed to packing effects.

Synthesis and Structural Characterization of 2D Polymer $[\{ Ge(CH_2SPh)_4\}(Cu_2I_2)\}_n]$ (3)

Auto-assembling processes between copper halides and thioether ligands display fascinating networks incorporating various copper halide clusters as core motifs. The growing interest in the preparation of such CuX-containing metal-organic frameworks is also due to promising photophysical properties of these materials, particularly those possessing tetranuclear cubane-like $Cu_4X_4L_4$ clusters [28-32]. The reaction of CuI with 0.5 equivalent of 1b in acetonitrile gave colorless crystals of $[\{ \{Ge(CH_2SPh)_4\}(CuI)_2\}_n]$ (3). Compound 3 crystallizes in the monoclinic crystal system $P2_1/n$. The single-crystal Xray diffraction study revealed the formation of a two-dimensional coordination polymer, constructed by dinuclear iodo-bridged copper units $Cu_2(\mu_2-I)_2$ linked by the tetrathioether Ge(CH₂SPh)₄ ligand in a μ -1 $\kappa^2 S$, S':2 $\kappa S''$:3 $\kappa S'''$ coordination mode. This arrangement is similar to that of the tetrathioether ligand Sn(CH₂SMe)₄ in the 1D coordination polymer $[{\{Sn(CH_2SMe)_4\}(ZnCl_2)_2\}_n}$ [17a]. Each copper(I) ion of the central dimeric Cu₂I₂ motif possesses a fourfold coordination to two iodine and two sulfur atoms, respectively, resulting in a distorted tetrahedral geometry. Interestingly, both copper(I) ions of this motif are differently coordinated by the thioether ligand **1b**. Whereas Cu(1) is ligated by two sulfur atoms of a single ligand molecule, Cu(2) is coordinated by two different ligands 1b, which are linked to the metal ion with only one sulfur atom (Figure 3, Table 2). The Cu-S bond lengths [2.3378(10) - 2.3731(13) Å] are close to those of related polymeric networks found in the literature. The Cu-Cu separation of 2.9433(9) Å reveals a guite loose non-bonding interaction between the two d^{10} ions in this polymeric net-



Figure 3. View of the core motif of $[\{\{Ge(CH_2SPh)_4\}(Cu_2I_2)\}_n]$ (3). The hydrogen atoms and phenyl groups are omitted for clarity.

Table 2. Selected bond length /Å and angles /° of **3**. Symmetry transformations used to generate equivalent atoms: #1 - x + 3/2, y + 1/2, -z + 1/2; #2 x - 1/2, -y + 3/2, z - 1/2; #3 x + 1/2, -y + 3/2, z + 1/2; #4 - x + 3/2, y - 1/2, -z + 1/2.

	-		
$\overline{Cu(1)-S(1)}$	2.358(1)	Cu(2)-I(2)	2.6210(7)
Cu(1) - S(2)	2.338(1)	Cu(1)-Cu(2)	2.9433(9)
Cu(2) - S(3)	2.361(1)		
Cu(2) - S(4)	2.373(1)	I(1) - Cu(1) - I(2)	111.65(3)
Cu(1) - I(1)	2.6580(7)	I(1) - Cu(2) - I(2)	110.62(3)
Cu(1) - I(2)	2.5775(6)	Cu(1) - I(1) - Cu(2)	67.39(2)
Cu(2) - I(1)	2.6471(6)	Cu(1) - I(2) - Cu(2)	68.96(3)

work. A somewhat closer contact of 2.862(2) Å was found in the dinuclear compound [{MeSi(CH₂SMe)₃}CuI]₂ [11b]. A distance of 2.8058(11) Å, which is close to the sum of the van der Waals radii of two copper atoms (2.8 Å) was encountered in the 2D metallopolymer [{(CuI)₂{(μ -PhS(CH₂)₂)SPh}}_n] [28a]. According to a survey of the Cambridge Structural Database, the mean value established for a variety of [Cu(μ -I)₂Cu] complexes amounts to ~ 2.76 Å [11b]. An example in the short range is given by a SMe₂-functionalized tetrathiafulvalene dinuclear Cu₂I₂ complex with a metal-metal separation of only 2.65 Å [14].

As illustrated in Figure 4, the 2D network of 3 consists of centrosymmetric 32-membered metallomacrocycles (constructed by four ligands and four Cu_2I_2 units) connected by centrosymmetric 12-membered rings. The latter cycles are constituted by two Cu(2) atoms which are linked by two bridging **1b** ligands. Further details of the crystal data and experimental parameters are presented in Table 3.

Table 3. Crystallographic data and details of the structure determination of **2b** and **3**.

	2b	3
Empirical formula	C28H28Br2GeHgS4	C ₂₈ H ₂₈ Cu ₂ GeI ₂ S ₄
Formula weight	925.74	946.21
Crystal system	triclinic	monoclinic
Space group	$P\overline{1}$	$P2_1/n$
a /Å	9.437(5)	14,628(3)
b /Å	13.364(5)	14.452(3)
c /Å	13.920(5)	15.883(3)
α /°	62.08(4)	90
β /°	89.78(6)	107.70(3)
γ /°	79.63(6)	90
Cell volume /Å ³	1519.2(12)	3198.7(11)
Z	2	4
Density (calculated), $Mg \cdot m^{-3}$	2.024	1.965
F(000)	884	1824
Size for single crystal /mm	$0.2 \times 0.2 \times 0.2$	0.4 imes 0.4 imes 0.2
Absorption coefficient μ /mm ⁻¹	2.024	4.460
Theta range for data collection /°	2.20 to 26.00	2.27 to 27.00
Index range	$-11 \le h \le 11$	$-18 \le h \le 18$
	$-16 \le k \le 16$	$-18 \le k \le 18$
	$-17 \le l \le 17$	$-20 \le l \le 20$
Reflections collected	14275	27045
Independent reflections	5604	6927
	[R(int) = 0.0399]	[R(int) = 0.0337]
Goodness of fit on F^2	1.015	1.050
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.03035$	$R_1 = 0.0304$
	$wR_2 = 0.0694$	$wR_2 = 0.0806$
R indices (all data)	$R_1 = 0.0374$	$R_1 = 0.0349$
	$wR_2 = 0.0714$	$wR_2 = 0.0834$



Figure 4. View on the *a*,*b* plane of the 2D sheet-like network of $[\{ Ge(CH_2SPh)_4\}(Cu_2I_2)\}_n]$ (3). Hydrogen atoms and phenyl groups are omitted for clarity.

Spectroscopic Properties of 1 and 3

The UV/Vis absorption spectra of the tetrathioether ligands **1a** and **1b** display both a maximum at 259 ($\varepsilon =$ 15600) and 261 nm ($\varepsilon =$ 14700 M⁻¹·cm⁻¹), respectively. These bands can be attributed to a mixture of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. After excitation at 260 nm of **1a** and **1b** in dichloromethane solution at room temperature (Figure 5), the emission maxima are observed at 341 and 333 nm, respectively. These fluorescence bands can be assigned to the lowest energy singlet state S₁ \rightarrow S₀ transition. Fluorescence quantum yields for **1a** ($\Phi = 0.08$) and for **1b** ($\Phi =$ 0.12) were determined using cresyl violet ($\Phi = 0.54$) as a fluorescence quantum yield standard [33]. Upon irradiation at 380 nm, compound **1b** exhibits in the solid state at 298 K an emission with a maximum at 440 nm (Figure 6), which is shifted to higher wavelength compared to the emission observed in CH_2Cl_2 . This emission is comparable with that observed for other dithioether ligands under similar conditions, originating probably from the excimer. The structureless emission band observed of **1b** in solid state at 77 K was not shifted and revealed no temperature dependence of the wavelength emission, i.e. no change of the energy for the emitting excited state. Unfortunately, the emission exhibited by polymer **3** in solid state at 298 K (Figure 7) is only moderate in intensity, and is most probably due to an emission centered on the ligand **1b** (*LC*). It seems that the important Cu···Cu separation, which is far above of sum of the van der Waals radii, excludes other excited state contribution such as *CC* or *XMLCT* (i.e. cluster-centered or halide-to-metal-to-ligand charge transfer).



Figure 5. Normalized emission spectra recorded for 1a (solid line) and 1b (dotted line) in CH₂Cl₂ at 298 K.



Figure 6. Normalized solid-state excitation (solid line) and emission (dotted line) spectra of 1b recorded at 298 K.

Synthesis of $[ReBr(CO)_3 \{Ge(CH_2SPh)_4\}]$ (4)

For comparison, we also reacted **1b** with the dinuclear compound $[{Re(\mu-Br)(CO)_3(THF)}_2]$ in CH₂Cl₂ solution at ambient temperature. IR monitoring showed, that within 1 h quantitative cleavage of the bromide bridges occurred affording the mononuclear compound fac-[ReBr(CO)_3{Ge(CH_2SPh)_4}] (4) in 76 % yield in form of an air-stable colorless solid (Scheme 2). In this chelate complex, two CH₂SPh arms are ligated on Re^I, the remaining two CH₂SPh arms are dangling. This structural proposition



Figure 7. Normalized solid-state excitation (solid line) and emission (dotted line) spectra of 3 recorded at 298 K.

is based on elemental analyses and the ¹H-NMR spectrum, which displays a singlet at $\delta = 2.70$ for the four methylene protons of the pendent CH₂SPh arms and two low-field shifted AX resonances at $\delta = 2.74$ and 3.79 assigned to the diastereotopic CH₂ groups of the rhenium-bound CH₂SPh arms. The observation of three strong ν (CO) vibrations corroborates the facial geometry of the three carbonyls around rhenium. Overall, the molecular structure of **4** is likely very similar to that of the structurally characterized chelate complex *fac*-[ReBr(CO)₃{(PhSCH₂)₂SiPh₂}] [21].

Conclusions

We have demonstrated that, unlike $C(CH_2SPh)_4$, the tetrathioether germane Ge(CH₂SPh)₄ coordinates to HgBr₂ and that the resulting metallopolymer 2b displays a onedimensional extended structure in the crystalline state. The intermolecular Hg-S contacts in 2b are markedly weaker than the intramolecular ones. In the case of CuI, a 2D polymer of composition $[{Ge(CH_2SPh)_4}(Cu_2I_2)]_n$ (3) is formed upon reaction with 1b in a 2:1 metal-to-ligand ratio. The presence of two pendent CH₂SPh arms in the mononuclear chelate compound fac-[ReBr(CO)₃{Ge(CH₂SPh)₄}] (4) appears promising to construct heterometallic systems by complexation of other metal ions on the two non-coordinated -SPh groups. Our ongoing systematic studies on the coordination chemistry of Si(CH₂SAr)₄ and Ge(CH₂SPh)₄ towards other copper, silver and mercury salts and various carbonyl compounds will be published elsewhere in the near future.



Scheme 2. Preparation of the mononuclear Re^I carbonyl complex 4.



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2105