Sterically Hindered Thiolato, Selenolato and Tellurolato Complexes of Mercury(II)†

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Mercury(II) complexes of sterically demanding arenechalcogenolato ligands, $Hg(EC_6H_2R_3\text{-}2,4,6)_2$ (E = S or Se; R = Me, Pr^i or Bu^t: E = Te; R = Me or Pr^i) have been prepared. Whereas complexes carrying smaller aryl substituents (R = Me) are polymeric, those with R = Pr^i and Bu^t form linear two-co-ordinate molecules. For a given R, the volatility of the complexes increases for E = S < Se < Te, while the thermal stability decreases in the same sequence. The preferred thermal decomposition pathway is reductive elimination to metallic mercury and the corresponding diaryl dichalcogenide. The oxidative addition of diaryl ditellurides to mercury and the reverse reaction are dependent on solvent polarity and steric factors; in the case of Te this leads to an unexpected decrease in stability with increased steric hindrance of the aryl substituents, R = Me > Pr^i ≫ Bu^t.

The chemistry of chalcogenolato complexes of Group 12 metals is dominated by the facile formation of co-ordination polymers.[1] As part of our search for single-component precursors for Group 12–16 solid-state materials we have however recently prepared chalcogenolato complexes in which this tendency is suppressed by substituents of high steric demand, resulting in low-co-ordinate molecular complexes which possess sufficiently high volatility to allow the deposition of Group 12–16 semiconductor films from the gas phase.[2] In the preceding paper[3] we have described some sterically hindered thiolates and selenolates of zinc and cadmium. We report here the synthesis and characterisation of arene-thiolato, -selenolato and -tellurolato compounds of mercury.

Whereas for zinc and cadmium the tendency to form non-molecular lattices is most pronounced for ligands with the least steric demand, the bonding situation for mercury is less straightforward. The strong tendency to form linear molecules X–Hg–X is exemplified by $Hg(SMe)_2$ and $Hg(SEt)_2$ which are both two-co-ordinate in the solid state,[4] with weak interactions between the $Hg(SR)_2$ units. By contrast, $Hg(SeMe)_2$ is polymeric,[5] as is $Hg(SBu^t)_2$[6] and its selenium analogue.[5a] Simple arenechalcogenolato complexes such as $Hg(SPh)_2$[7] and $Hg(SePh)_2$[8] are also polymeric, as indicated by their low solubility in non-co-ordinating solvents, but are readily solubilised by the addition of donor ligands such as phosphines.[9] It was therefore of interest to us to prepare a range of mercury complexes of ligands containing S, Se and Te with varying degrees of steric hindrance. Some mercury complexes of bulky trialkylsilyl-substituted thiolate ligands have recently been described as models for the bonding of mercury in proteins.[10]

Results and Discussion

Chalcogenolato complexes of mercury are generally accessible *via* three alternative methods [equations (1)–(3)]. Methods (1) and (2) have the advantage of yielding compounds free of ionic impurities under very mild reaction conditions and are therefore preferred in the present work. The ligands employed are

$$Hg[N(SiMe_3)_2]_2 + 2\,REH \longrightarrow Hg(ER)_2 + 2\,NH(SiMe_3)_2 \quad (1)$$

$$Hg + R_2E_2 \longrightarrow Hg(ER)_2 \quad (2)$$

$$HgX_2 + 2\,LiER \longrightarrow Hg(ER)_2 + 2\,LiX \quad (3)$$

(R = aryl; E = S, Se or Te)

$2,4,6\text{-}Me_3C_6H_2E^-$ (R^1E^-), $2,4,6\text{-}Pr^i{}_3C_6H_2E^-$ (R^2E^-) and $2,4,6\text{-}Bu^t{}_3C_6H_2E^-$ (R^3E^-) (E = S, Se or Te).

Thiolato Complexes.—The reaction of 2,4,6-trimethylbenzenethiol with mercury bis[bis(trimethylsilyl)amide] in light petroleum leads to the precipitation of $Hg(SR^1)_2$ **1** as a colourless fibrous crystalline solid. The compound is soluble in pyridine and to a lesser degree in hot toluene; it does not sublime and decomposes at 230 °C. The polymeric nature is confirmed by the infrared spectrum which shows several bands due to Hg–S stretching modes in the 500–200 cm^{-1} region (Table 1); it resembles in this respect the parent compound, $Hg(SPh)_2$.[7b] Attempts to record Raman spectra were unsuccessful and led to decomposition. On heating in a sealed tube, $Hg(SR^1)_2$ first decomposes to metallic mercury and dimesityl disulphide; above 400 °C the two components react to give HgS.

The analogous protolysis of the mercury amido complex using the sterically more hindered tris(isopropyl)benzenethiol gives a clear solution from which colourless crystals of $Hg(SR^2)_2$ **2** are obtained in high yield. The compound shows good solubility in non-polar solvents. During the course of this work the independent preparation of this compound by two other research groups and the X-ray structure have been reported;[10,11] the latter confirms that **2** is monomeric in the solid state.

The compound $Hg(SR^3)_2$ **3** is obtained according to equation (1) as a white microcrystalline solid which is readily sublimable, soluble in non-co-ordinating solvents and monomeric in benzene and in the solid state.

Selenolato Complexes.—The compound $Hg(SeR^1)_2$ **4** was prepared according to equation (2) by stirring mercury with a solution of the diaryl diselenide in toluene. The reaction is facile and quantitative. The product, a white solid, is less soluble in pyridine than the sulphur analogue **1** but sublimes at 200 °C (0.001 mm Hg). It is thought to have a polymeric structure resembling that of **1**.

The compound $Hg(SeR^2)_2$ **5** was prepared according to equations (1)–(3) from the selenol, by oxidative addition of

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† *Non-SI unit employed:* mm Hg ≈ 133 Pa.

Table 1 Raman and infrared data (cm^{-1}) for monomeric mercury chalcogenolates in the region 620–100 cm^{-1}. Infrared data in parentheses

$Hg(SR^2)_2$ **2**	$Hg(SeR^2)_2$ **5**	$Hg(SR^3)_2$ **3**	$Hg(SeR^3)_2$ **6**
614vw	606w	606m	
572w	567w	569wm	576m
521w	516w		
485w	478vw	490w	481w
431w	442w	449vw	
406w	(403m)	414w	396w
(404w)	400vw		
(372s) ν_{asym}(M–S)		(378vs) ν_{asym}(M–S)	
(350s) ν_{asym}(M–S)	355vw	361m	
		332s ν_{sym}(M–S)	334w
320vs ν_{sym}(M–S)			
(273w)		273w(br)	
270w	269m		(270m) ν_{asym}(M–Se)
	(265vs) ν_{asym}(M–Se)		
		254w(br)	254m
	(230w)		(230w)
	214s ν_{sym}(M–Se)		214m
193w	181vs ν_{sym}(M–Se)		187s ν_{sym}(M–Se)
173vw		169vw	166m
140m	135m	142m	142m

$R^2{}_2Se_2$ to Hg in light petroleum, and from $HgCl_2$ and $LiSeR^2$ in tetrahydrofuran (thf). It forms pale yellow crystals which are more volatile than the sulphur analogue and sublime at 93 °C (0.01 mm Hg). Because of instability in solution over prolonged periods of time NMR spectra had to be recorded at −20 °C. Although NMR, IR and Raman data confirm **5** as a monomer, only a very broad ^{77}Se signal was obtained which broadened further on cooling, possibly as a result of ligand-exchange processes. The facile exchange of PhSe ligands has previously been demonstrated for $Hg(SePh)_2$.[12] Whereas compounds **1**–**4** do not show appreciable sensitivity to light, **5** readily darkens even in diffuse daylight, to give metallic mercury and diaryl diselenide. The same decomposition pathway is induced by the attempt to recrystallise **5** from warm light petroleum or chloroform; the selenium complex is evidently much less stable towards reductive elimination than are sulphur complexes.

The reaction of $HgCl_2$ with $LiSeR^3$ affords pale yellow crystals of $Hg(SeR^3)_2$ **6**.* As expected by comparison with **5**, the compound is a sublimable monomer which readily dissolves in non-co-ordinating solvents. It is however significantly less light sensitive and thermally more stable than is **5**; the reason for this difference is not clear. Compound **6** decomposes in hot toluene slowly to Hg and $R^3{}_2Se_2$.

Tellurolato Complexes.—The compound $R^1{}_2Te_2$ in toluene readily adds to mercury to give $Hg(TeR^1)_2$ **7** as dark yellow crystals. The same compound is obtained in a fast low-temperature reaction between $Hg[N(SiMe_3)_2]_2$ and the recently isolated R^1TeH,[14] and *via* the comparatively slow room-temperature reaction between $Hg[N(SiMe_3)_2]_2$ and $R^1{}_2Te_2$ [equation (4)]. The formation of $N_2(SiMe_3)_4$[15] as a possible

$$Hg[N(SiMe_3)_2]_2 + R^1{}_2Te_2 \longrightarrow Hg(TeR^1)_2 + \cdots \quad (4)$$

by-product of this reaction could not be confirmed, and the mechanism is unclear. The analogous amides of zinc and cadmium do not react with ditellurides in this way.

The limited solubility of **7** suggests a high degree of association, although the complex is noticeably more volatile than the analogous complexes of S and Se described above and sublimes without decomposition at 184 °C (0.01 mm Hg). Further heating generates mercury and $R^1{}_2Te_2$. Few examples of mercury tellurolates have been reported, *e.g.* $Hg(TeC_6H_4\text{-}R\text{-}4)_2$ (R = H,[8b,9] OEt[16] or Me[17]) and some alkyl[9,18] and fluoroalkyl[19] complexes, as well as a number of cluster cations[20] and anions.[21]

Attempts to extend reaction (2) to the sterically more hindered isopropyl-substituted ditelluride $R^2{}_2Te_2$ in analogy to the formation of **7** met with little initial success. The reaction is very solvent dependent and does not proceed in toluene or light petroleum. Oxidative addition to mercury does, however, take place in polar solvents such as methanol at room temperature to give $Hg(TeR^2)_2$ **8** as a yellow solid. The reverse reaction is readily induced by warming **8** in methanol, or by the attempted recrystallisation of the compound in non-polar solvents, although **8** can be recrystallised from acetonitrile as orange needles which decompose at *ca.* 75 °C.

Although there is no direct evidence, the pronounced solvent effect on the oxidative addition of $R^2{}_2Te_2$ to mercury may point towards a mechanism involving a heterolytic rather than a homolytic Te–Te bond scission, reminiscent of the mechanism of bromination of C=C double bonds in polar media *via* Br^+ and Br^-.[22] A cation R^2Te^+ would be expected to exhibit a higher reactivity and overcome steric hindrance more easily than a neutral ditelluride adsorbed onto the surface of mercury metal prior to the addition step.

Although air-stable, compound **8** is unusually sensitive to warming and to slight pressure, and even scratching the solid with a spatula induces it to revert to $R^2{}_2Te_2$ and metallic mercury. For this reason, Nujol mulls could not be prepared, although a diffuse-reflectance infrared spectrum was obtained in the region 4000–600 cm^{-1}.

It is well known that the oxidative addition of diaryl dichalcogenides to mercury is temperature-dependent and readily reversible [equation (5)]. In the case of E = S, shifting

$$Hg(ER)_2 \rightleftharpoons Hg + RE\text{–}ER \quad (5)$$

the equilibrium to the right requires high temperatures[7a] but becomes increasingly more facile in the sequence E = S < Se < Te, following the trend indicated by the M–X bond strengths in diatomic molecules;[23] Hg–S, 213; Hg–Se, ⩽167; Hg–Te, ⩽142 kJ mol^{-1}. However, the stability of sterically less-hindered arenetellurolates underlines the importance of steric factors as the driving force for reductive elimination. Far from providing additional kinetic stability, bulky *ortho* substituents R in $2,4,6\text{-}R_3C_6H_2Te^-$ labilise the metal complexes with respect to reductive elimination in the sequence R = Me > Pr^i ≫ Bu^t.

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* *Note added at proof:* Since the submission of this paper a preliminary report on an alternative synthesis of this compound has appeared.[13]

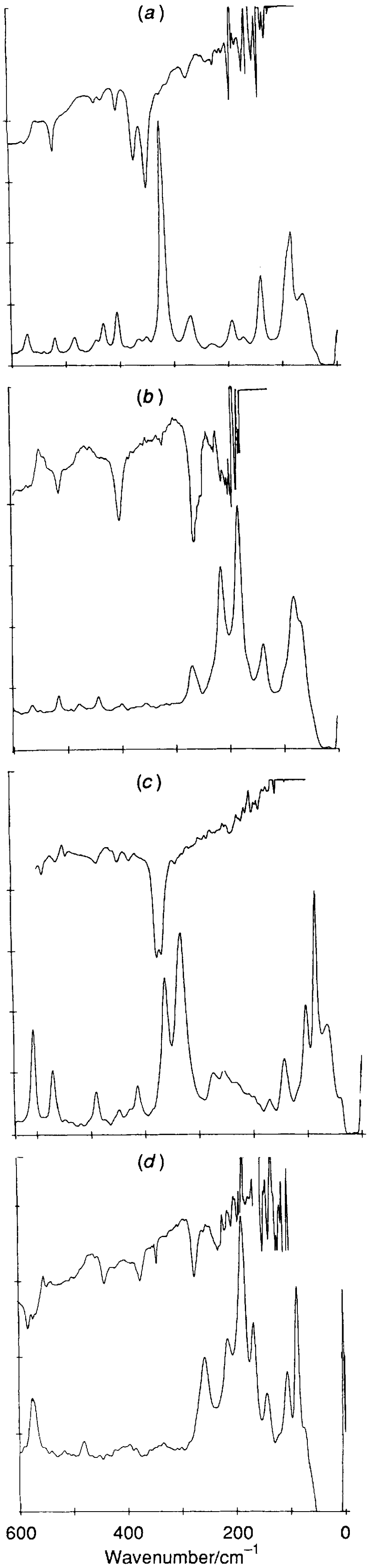

Fig. 1 Infrared (upper) and Fourier-transform Raman spectra (lower) of mercury chalcogenolato complexes: (*a*) Hg(SR^2)$_2$ **2**, (*b*) Hg(SeR^2)$_2$ **5**, (*c*) Hg(SR^3)$_2$ **3** and (*d*) Hg(SeR^3)$_2$ **6**

Table 2 Mercury-199 NMR data

Compound	δ(^{199}Hg)	Half-width (Hz)
1 Hg(SR^1)$_2$^{a}	−1044	10
2 Hg(SR^2)$_2$^{b}	−1111	16
3 Hg(SR^3)$_2$^{b}	−1274	6
4 Hg(SeR^1)$_2$^{a}	−1486	18
5 Hg(SeR^2)$_2$^{b}	−1570^c	71
6 Hg(SeR^3)$_2$^{b}	−1734	8

^{a} Measured at 15.9 MHz, in [$^2H_5$]pyridine solution, 29 °C, relative to neat HgMe$_2$. ^{b} In CDCl$_3$ solution, 0.5 mol dm^{-3}. ^{c} At −20 °C.

It is to be expected that the same forces operate in the thiolato and selenolato complexes but are less apparent because of the higher activation barrier towards elimination. Apparently, only in the case of the relatively weak Hg–Te bond can the equilibrium easily be driven either way by such subtle influences as pressure or polarity changes of the reaction medium.

In agreement with the stability trend observed for **7** and **8**, efforts to prepare the *tert*-butyl-substituted compound Hg(TeR^3)$_2$ by oxidative addition of R$^3{}_2$Te$_2$ in any solvent, including methanol, pyridine and acetonitrile, or by the reaction of HgCl$_2$ with LiTeR^3 have been unsuccessful.

Vibrational Spectroscopy.—The vibrational frequencies of complexes **2**, **3**, **5** and **6** are given in Table 1 and Fig. 1. The mesityl complexes and the mercury tellurides were unstable in the Raman beam, even though a low-intensity near-infrared laser was used as the light source. The IR spectrum of **1** shows bands at 320 and 295 cm^{-1}, while the metal–chalcogenide vibrations of **4** and **7** occur below 200 cm^{-1} and could not be measured.

For linear molecules X–M–X, two non-coincident M–X stretching modes are expected in the infrared and Raman spectra, respectively. The Raman spectrum of **2** shows a single strong band for ν_{sym}, while the IR spectrum consists of two bands at 350 and 372 cm^{-1}; this splitting is likely to be caused by mixing with overtones or combinations of other low-frequency modes. A similar mixing occurs in the Raman spectrum of **5**. The Raman spectrum of Hg(SR^3)$_2$ **3** in the M–X region consists of two bands at 361m and 332s cm^{-1}. Comparison with the spectrum of [{Cd(SR^3)$_2$}$_2$]^3 suggests that the former is associated with a vibrational mode of the aryl substituent, enhanced by the proximity of the symmetric Hg–S stretch. The position of the latter band agrees well with ν_{sym} of **2** at 320 cm^{-1}.

The symmetric and antisymmetric Hg–E stretching modes (E = S or Se) typically occur at significantly higher frequencies than those previously reported[23] for polymeric thiolato complexes, as expected. The simplicity of the spectra and the high values of the Hg–E stretching modes, compared to the corresponding frequencies of the related dimeric zinc and cadmium complexes,[3] confirm the monomeric structure of the mercury chalcogenolates.

^{199}Hg *NMR Spectroscopy*.—The mesityl complexes are soluble only in co-ordinating solvents and were recorded in pyridine; they exist in solution presumably as tetrahedral adducts (Table 2), although there is no significant chemical shift difference between these adducts and the more highly substituted complexes **2**, **3**, **5** and **6** which were recorded in chloroform solution. The two selenolato complexes exhibit signals which are high-field shifted by *ca.* 460 ppm compared to the corresponding thiolates, while Bu^t substituents induce a high-field shift of *ca.* 160 ppm compared to Pr^i substituents. These data significantly extend the chemical shift range previously observed for chalcogenolato complexes. Our value for **2** compares well with that recently reported for this compound at a lower concentration (δ −1079.55[10]). The signals due to the more hindered compounds Hg(ER^3)$_2$ (E = S

Table 3 Analytical and physical data for mercury chalcogenolato complexes

				Analysis (%)[a]		
Complex	Yield (%)	M.p. (°C)	Colour	C	H	S
1	75	230[b]	White	42.9 (43.0)	4.4 (4.4)	12.9 (12.8)
2	95	140	White	53.7 (53.8)	6.9 (6.7)	9.6 (9.6)
3	69	270[b]	White	56.9 (57.2)	7.7 (7.7)	8.1 (8.5)
4	75	200[c]	White	36.2 (36.1)	3.6 (3.7)	
5	90	133	Pale yellow	47.2 (47.1)	5.8 (6.0)	
6	74	150[c]	Pale yellow	51.2 (50.9)	6.9 (6.9)	
7	70	215[b]	Deep yellow	31.1 (31.2)	3.2 (3.2)	
8	90[d]	75[b]	Yellow-orange	41.9 (41.8)	5.4 (5.4)	

[a] Required values given in parentheses. [b] With decomposition. [c] Sublimation temperature, 0.01 mm Hg. [d] Before recrystallisation, see Experimental section.

Table 4 Proton NMR data for mercury chalcogenolato complexes, $Hg(EC_6H_2R_3\text{-}2,4,6)_2$

Complex	R	E	*o*-R	*p*-R	Aryl
1[a]	Me	S	2.57 (s, 6 H)	2.17 (s, 3 H)	6.80 (s, 2 H)
2[b]	Pr^i	S	1.08 (d, 12 H) 4..00 (spt, 2 H)	1.20 (d, 6 H, CH*Me*$_2$) 2.80 (spt, 1 H, *C*HMe$_2$, $J = 7$)	6.80 (s, 2 H)
3[b]	Bu^t	S	1.80 (s, 18 H)	1.52 (s, 9 H)	7.40 (s, 2 H)
4[a]	Me	Se	2.62 (s, 6 H)	2.20 (s, 3 H)	6.84 (s, 2 H)
5[c]	Pr^i	S	1.13 (d, 12 H) 4.17 (spt, 2 H)	1.38 (d, 6 H, CH*Me*$_2$) 3.07 (spt, 1 H, *C*HMe$_2$, $J = 7$)	7.15 (s, 2 H)
6[b]	Bu^t	Se	1.67 (s, 18 H)	1.40 (s, 9 H)	7.55 (s, 2 H)
7[a]	Me	Te	2.62 (s, 6 H)	2.20 (s, 3 H)	6.84 (s, 2 H)

s = Singlet, d = doublet, spt = septet; *J* in Hz.
[a] In [$^2H_5$]pyridine solution, 60 MHz, 35 °C. [b] In $CDCl_3$ solution. [c] In $CDCl_3$ solution, −20 °C.

Table 5 Carbon-13 NMR data for mercury chalcogenolates, $Hg(EC_6H_2R_3\text{-}2,4,6)_2$*

$Hg(SR^2)_2$ **2**	$Hg(SR^3)_2$ **3**	$Hg(SeR^3)_2$ **6**	Assignment
123.4	126.5		*ipso*-C
152.4	154.1	154.7	*ortho*-C
121.3	122.3	122.3	*meta*-C
148.7	149.0	149.2	*para*-C
34.8			*ortho*-*C*HMe$_2$
24.1			*ortho*-CH*Me*$_2$
34.1			*para*-*C*HMe$_2$
23.8			*para*-CH*Me*$_2$
	38.1	38.8	*ortho*-*C*Me$_3$
	32.0	32.5	*ortho*-C*Me*$_3$
	34.9	34.9	*para*-*C*Me$_3$
	31.5	31.5	*para*-C*Me*$_3$

* In $CDCl_3$ solution, 22.5 MHz, 28 °C.

or Se) are narrow, whereas $Hg(SR^2)_2$ **2** shows slight broadening. By contrast, the analogous selenium complex **5** gives rise to a broad signal at −20 °C (half-width 71 Hz) which broadens further on cooling and is thought to be the result of ligand-exchange processes, although detailed studies on this rather labile compound proved difficult. The ^{77}Se NMR spectrum of **5** also shows a very broad signal. Ligand exchange should be more facile for Se than for S, in line with the trends in bond strengths, but would be disfavoured for the sterically highly hindered *tert*-butyl compound; in agreement with this assumption it is not detected for **3** and **6**.

Conclusion

In cases where steric hindrance is moderate, arenechalcogenolato complexes of mercury, $Hg(EC_6H_2R_3\text{-}2,4,6)_2$, exist as co-ordination polymers (R = Me), although the corresponding compounds are more volatile and soluble than related complexes of Zn and Cd.[3] The volatility of the mesityl derivatives $Hg(ER^1)_2$ increases for E = S < Se < Te, reflecting the decreasing Hg–E bond strengths in this sequence. The thermal stability decreases in the same sequence. Complexes carrying *ortho*-Pr^i and -Bu^t groups are linear, two-co-ordinate monomers. Tellurium complexes are strongly destabilised by bulky *ortho* substituents R: whereas $Hg(TeR^1)_2$ (R = Me) is thermally stable at *ca.* 180 °C, $Hg(TeR^2)_2$ (R′ = Pr^i) is at its stability limit under ambient conditions, and complexes with R = Bu^t cannot be made. The favoured decomposition pathway is the reductive elimination to Hg metal and diaryl dichalcogenide; this limits the usefulness of these compounds as precursors to Group 12–16 solid-state materials *via* thermolysis. Photolytic decomposition methods are being studied.

Experimental

All experiments were carried out under argon using standard vacuum-line techniques. Solvents were distilled under nitrogen from sodium–benzophenone [diethyl ether, thf, light petroleum (b.p. 40–60 °C)], sodium (toluene) or calcium hydride (dichloromethane, acetonitrile). The NMR solvents were stored over 4Å molecular sieve under argon and degassed by several freeze–thaw cycles. The compounds 2,4,6-Me$_3$C$_6$H$_2$SH (R^{1}SH),[25] 2,4,6-Pr$^i_3$-C$_6$H$_2$SH (R^{2}SH),[25] 2,4,6-Bu$^t_3$C$_6$H$_2$SH (R^{3}SH),[26] 2,4,6-Me$_3$C$_6$H$_2$SeH (R^{1}SeH),[3] 2,4,6-Pr$^i_3$C$_6$H$_2$SeH (R^{2}SeH),[3] 2,4,6-Bu$^t_3$C$_6$H$_2$SeH (R^{3}SeH),[2] (2,4,6-Me$_3$C$_6$H$_2$Te)$_2$ (R$^1_2$Te$_2$),[27] (2,4,6-Pr$^i_3$C$_6$H$_2$Te)$_2$ (R$^2_2$Te$_2$)[14] and Hg[N(SiMe$_3$)$_2$]$_2$[28] were prepared as described. Melting points are uncorrected. Infrared spectra were recorded on Mattson Polaris, Nicolet F20 and Perkin-Elmer 684 spectrometers, Raman spectra on a Bruker IFS-66 instrument equipped with a FRA 106 FT-Raman module, and NMR spectra on JEOL PMX-60 (^{1}H) and EX90Q (^{1}H, ^{13}C, ^{199}Hg) instruments.

The mercury complexes described were prepared either by protolysis of the mercury amide, from $HgCl_2$ by halide exchange, or by oxidative addition of the dichalcogenide to metallic mercury. One representative example for each method is given below. Analytical, ^1H and ^{13}C NMR data are given in Tables 3, 4 and 5, respectively.

$Hg(SR^3)_2$ **3**.—To a solution of R^3SH (0.5 g, 1.8 mmol) in light petroleum (20 cm^{-3}) was added *via* syringe at room temperature a solution of $Hg[N(SiMe_3)_2]_2$ (0.53 g, 0.9 mmol) in light petroleum (5 cm^{-3}). The mixture was stirred for 2 h, filtered, and the residue recrystallised from toluene at −20 °C to obtain the product as white microcrystals, 0.47 g (0.62 mmol, 69%), m.p. 170 °C. The compounds $Hg(SR^1)_2$ **1**, $Hg(SR^2)_2$ **2** and $Hg(SeR^2)_2$ **5** were prepared similarly.

$Hg(SR^3)_2$ **6**.—A solution of $LiSeR^3$ in thf was prepared by treating $R^3{}_2Se_2$ (0.50 g, 0.77 mmol) with 2 equivalents $LiBHEt_3$ at room temperature. After 30 min a small quantity of ethanol was added to destroy excess of $LiBHEt_3$. To this mixture was added $HgCl_2$ (0.20 g, 0.77 mmol) at room temperature. After stirring for 2 h the solvent was removed *in vacuo*, the product extracted into toluene and obtained as pale yellow crystals at −20 °C (0.48 g, 0.57 mmol, 74%).

$Hg(TeR^2)_2$ **8**.—Mercury (0.3 g, 1.5 mmol) was stirred with a suspension of $R^2{}_2Te_2$ (1.0 g, 1.51 mmol) in methanol (20 cm^{-3}) at room temperature for 24 h. A yellow-orange powder precipitated which was filtered off, washed with methanol and dried *in vacuo* (1.16 g, 1.35 mmol, 90%). A quantity (0.1 g) of this material was recrystallised from acetonitrile (5 cm^{-3}) to give orange needle-like crystals, contaminated with a small quantity of $R^2{}_2Te_2$, which were separated manually. They are unstable in non-polar solvents and poorly soluble in polar media. Because of the sensitivity of the compound towards elimination of metallic mercury, reliable NMR data were not obtained. The compounds $Hg(SeR^1)_2$ **4** and $Hg(TeR^1)_2$ **7** were similarly obtained from the dichalcogenides, using toluene as reaction medium.

$Hg(TeR^1)_2$ *from* R^1TeH.—To a solution of R^1TeH (2 mmol) at −20 °C, was added *via* syringe a solution of $Hg[N(SiMe_3)_2]_2$ (0.52 g, 1.0 mmol) in light petroleum (5 cm^{-3}). A yellow precipitate formed immediately. The mixture was warmed to room temperature, filtered, and the residue recrystallised from hot toluene (0.45 g, 0.65 mmol, 65%).

$Hg(TeR^1)_2$ *from* $R^1{}_2Te_2$.—A solution of $Hg[N(SiMe_3)_2]_2$ (0.52 g, 1.0 mmol) in light petroleum at room temperature was treated with $R^1{}_2Te_2$ (0.51 g, 1.03 mmol) and stirred for 15 min. A yellow precipitate of **8** formed which was identical to previously obtained samples. A similar reaction at −20 °C proceeded only very slowly.

Acknowledgements

This work was supported by the SERC and the Royal Signals and Radar Establishment, Great Malvern. We are grateful to Dr. J. E. Hails for helpful discussions and to Dr. D. Williamson for assistance with the NMR measurements.

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Received 20*th December* 1990; *Paper* 0/05725H