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On the synthesis and structural analysis of some coordination polymers derived from $Hg(TeAr)_2$ involving dithio ligands

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ABSTRACT

$Hg(TePh)_2$ (Ph = phenyl) reacts with $Hg(dedtc)_2$ (dedtc = diethyldithiocarbamate), as well as with $Hg(dedtp)_2$ (dedtp = diethyldithiophosphate) and sodium pyrrolidine dithiocarbamate to give the coordination polymers $[Hg(TePh)(S_2CNEt_2)]_n$ (**1**), $[Hg(TePh)\{S_2P(OEt)_2\}]_n$ (**2**), and $[Hg(TePh)(S_2CNC_4H_8)]_n$ (**3**); $Hg\{Te(dmb)\}_2$ (dmb = 2,6-dimethoxybenzene) and $Hg\{Te(mes)\}_2$ (mes = 2,4,6-trimethylbenzene) react with $NaS_2CNC_4H_8$ to yield the polymers $[Hg\{Te(dmb)(S_2CNC_4H_8)\}]_n$ (**4**) and $[Hg\{Te(mes)(S_2CNC_4H_8)\}]_n$ (**5**), as well as the mononuclear complexes $[Hg(dmb)(S_2CNC_4H_8)]$ (**6**) and $[Hg(mes)(S_2CNC_4H_8)]$ (**7**). The compounds **1**, **2** and **3** present a helical structure along the Hg–Te bonds, while **4** and **5** show a zigzag arrangement. In **3**, **4** and **5** each Hg atom is linked to two sulfur atoms of one dithio ligand. Compounds **6** and **7** are mononuclear, and probably also decomposition products of **4** and **5**, respectively.

1. Introduction

Newly we have pointed out, in a kind of review works on recent results on Hg–E clusters [1,2], that the compounds $Hg(EPh)_2$ (E = Se, Te; Ph = phenyl) are valuable sources of {ME} for the synthesis of binary and ternary clusters, attaining also polymeric structures by intermolecular $Hg\cdots E$ interactions in the solid state [3–5], being solubilized only in coordinating solvents [6]. This class of compounds has been extensively used for the well-designed syntheses of binary, as well as ternary clusters, acting as templates to generate new products [4,7,8]. Given our interest in the metal organochalcogenide cluster chemistry, we have investigated the reactions of $Hg(EPh)_2$ in different chemical environments and with diverse reagents. These results led to several publications which are listed in the first two references of this article.

With regard to coordination polymers (CP), in the last decades it has been observed an increase involving studies on their synthesis and structural characterization, since these species can be viewed as an interface between synthetic chemistry and material sciences. Coordination polymers attain specific structures, properties and reactivities, which are not present in mononuclear compounds, justifying the efforts put worldwide in the search for new materials (CP) in different areas such as catalysis, molecular sensing, magnetism and luminescence, for instance [9].

However, despite its potential applications [9], CP of mercury have been less investigated in comparison to other elements, because these species (Hg–CP) present very low solubility in organic solvents and also in water. This undesirable property can lead to serious problems regarding the effective reactivity as well as the adequate growth of crystals suitable for X-ray measurements [9,10]. Another solubility limiting factor is the absence of mercury aryl chalcogenolate polymers with substituted aryl groups: the only known compounds of mercury aryl chalcogenolate polymers are those derived from $Hg(PhE)_2$.

With the aim, to show that $Hg(TePh)_2$ and its substituted analogue compounds $Hg(TeAr)_2$ {Ar = 2,4,6-trimethylbenzene (mes); 2,6-dimethoxybenzene (dmb)} are valuable sources for the preparation of proper coordination polymers by reaction with dithio ligands, because the substituted aryl groups improve the solubility of the resulting CPs, we carried out a series of reactions of $Hg(TePh)_2$ with the dithiocarbamate $NaS_2CNC_4H_8$, as well as with $Hg(dedtp)_2$ (dedtp = diethyldithiophosphate) and $Hg(dedtc)_2$ (dedtc = diethyldithiocarbamate). With the bulky species $Hg\{Te(dmb)\}_2$ and $Hg\{Te(mes)\}_2$, reactions were carried out only with $NaS_2CNC_4H_8$, because their reactions with $Hg(dedtp)_2$ and $Hg(dedtc)_2$ do not occur under normal conditions.

We discuss in follows the synthesis and the structural characterization of the coordination polymers $[Hg(TePh)(S_2CNEt_2)]_n$ (**1**), $[Hg(TePh)\{S_2P(OEt)_2\}]_n$ (**2**), $[Hg(TePh)(S_2CNC_4H_8)]_n$ (**3**), $[Hg\{Te(dmb)(S_2CNC_4H_8)\}]_n$ (**4**), $[Hg\{Te(mes)(S_2CNC_4H_8)\}]_n$ (**5**), as well as the mononuclear compounds $[Hg(dmb)(S_2CNC_4H_8)]$ (**6**) and $[Hg(mes)(S_2CNC_4H_8)]$ (**7**).

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2. Experimental

2.1. General

Solvents were purified and dried according to literature procedures [11] and freshly distilled before use. Since the chalcogenophilicity of mercury increases in the sequence S < Se < Te [12] and this has been considered as one of the factors for the danger of organometallic mercury species, the manipulation of the HgTe-containing chemicals was made in a good hood and with a paper gas mask and gloves. Elemental analyses (CHN) were carried out with a VARIO EL (Elementar Analysensysteme GmbH) analyzer. Infrared spectra were measured on a Bruker Tensor 27 mid-IR spectrometer. Melting points were determined on a Microquímica MQAPF-301 melting point apparatus and are uncorrected.

The reaction steps involved in the preparation of the compounds referred in this work are summarized in Chart 1.

2.2. Preparation of [Hg(TePh)(S_2CNEt_2)]$_n$ (**1**)

To 0.061 g (0.1 mmol) of Hg(PhTe)$_2$ dissolved in 8 mL of dimethylformamide (dmf), 0.05 g (0.1 mmol) of Hg(dedtc)$_2$ were added. After 1 h stirring at 40 °C a clear, light brown solution was formed. Yellow crystals of the product grew over the course of 4 days. Yield: 89% based on Hg(PhTe)$_2$.

Properties: Air stable, yellow crystalline substance. Melting point: 143–146 °C. *Anal.* Calc. for $C_{11}H_{15}HgNS_2Te$ (553.55): C, 23.87; H, 2.73; N, 2.53. Found: C, 23.91; H, 2.78; N, 2.58%. IR (KBr): 3045 [ν_s(C–H)]; 1568 [ν_s(C═C)]; 1074 [δ_{ip}(C═C–H)]; 730 [δ_{op}(C═C–H)]; 437 [δ_{op}(C═C–C)]; 2924 [ν_s(C–H)$_{aliph.}$]; 1264[ν_s(C–N)]; 838 [ν_s(C–S)]; 1202 cm^{-1} [ν_s(C═S)]. (δ_{ip} and δ_{op} = in-plane and out-of-plane bendings, respectively).

2.3. Preparation of [Hg(TePh){$S_2P(OEt)_2$}]$_n$ (**2**)

To 0.061 g (0.1 mmol) of Hg(PhTe)$_2$ dissolved in 8 mL of dmf, 0.057 g (0.1 mmol) of Hg(dedtp) were added. After 1 h stirring at 40 °C a clear, dark yellow solution was formed. Yellow crystals of the product were obtained in the course of 6 days. Yield: 85% based on Hg(PhTe)$_2$.

Properties: Yellow crystalline substance. Melting point: 152–154 °C. *Anal.* Calc. for $C_{30}H_{45}Hg_3O_6P_3S_6Te_3$ (1771.50): C, 20.34; H, 2.56. Found: C, 20.52; H, 2.62%. IR (KBr): 3052 [ν_s(C–H)]; 2894 [ν_s(C–H)$_{aliph.}$]; 1570 [ν_s(C═C)]; 1096 [δ_{ip}(C═C–H)]; 940 [ν_s(C–O)]; 778 [ν_s(P–O)]; 738 [δ_{op}(C═C–H)]; 691 [ν_s(P═S)]; 557 [ν_s(P–S)]; 453 cm^{-1} [δ_{op}(C═C–C)].

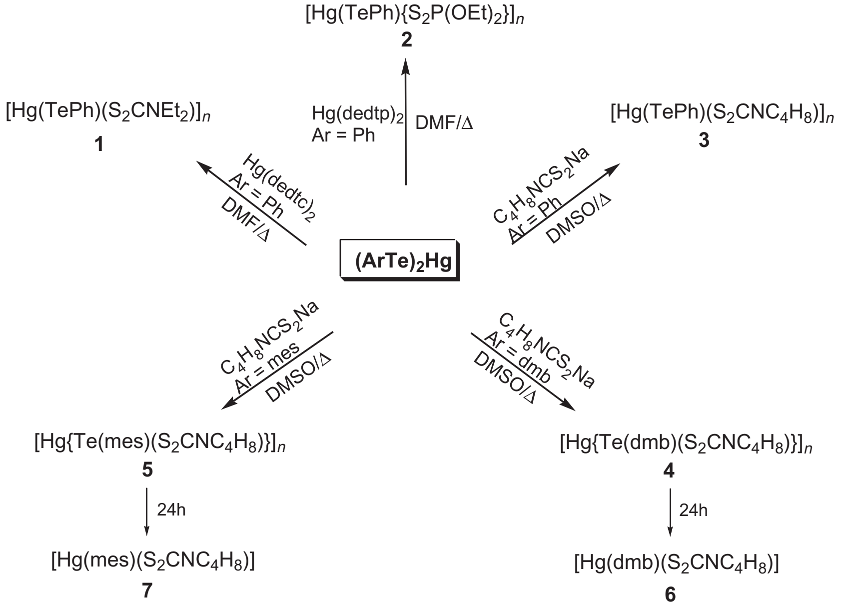
2.4. Preparation of [Hg(TePh)($S_2CNC_4H_8$)]$_n$ (**3**)

To 0.061 g (0.1 mmol) of Hg(PhTe)$_2$ dissolved in 8 mL of dimethyl sulfoxide (DMSO), 0.017 g (0.1 mmol) of sodium pyrrolidine dithiocarbamate were added. After 1 h stirring at 40 °C a clear, brown solution was formed. Orange crystals of the product were obtained over the course of 9 days. Yield: 78% based on Hg(PhTe)$_2$.

Properties: Air stable, orange crystalline substance. Melting point: 203–205 °C. *Anal.* Calc. for $C_{11}H_{13}HgNS_2Te$ (551.53): C, 23.95; H, 2.38; N, 2.54. Found: C, 23.93; H, 2.42; N, 2.43%. IR (KBr): 3000 [ν_s(C–H)]; 1568 [ν_s(C═C)]; 1249 [ν_s(C–N)]; 1166 [ν_s(C═S)]; 1013 [δ_{ip}(C═C–H)]; 943 [ν_s(C–S)]; 729 [δ_{op}(C═C–H)]; 450 cm^{-1} [δ_{op}(C═C–C)].

2.5. Preparation of [Hg{Te(dmb)($S_2CNC_4H_8$)}]$_n$ (**4**)

To 0.073 g (0.1 mmol) of Hg{Te(dmb)}$_2$ dissolved in 6 mL of DMSO, 0.017 g (0.1 mmol) of sodium pyrrolidine dithiocarbamate were added. After 1 h stirring at 40 °C a brown solution was



dmb = 2,6-dimethoxybenzene
mes = 2,4,6-trimethylbenzene
dedtc = diethyldithiocarbamate
dedtp = diethyldithiophosphate

Chart 1.

Table 1
Crystallographic data and refinement parameters for **1**, **2**, **3**, **4** and **5**.

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{11}H_{15}HgNS_2Te$	$C_{30}H_{45}Hg_3O_6P_3S_6Te_3$	$C_{11}H_{13}HgNS_2Te$	$C_{26}H_{34}Hg_2N_2O_4S_4Te_2$	$C_{14}H_{19}HgNS_2Te$
Fw (g mol^{-1})	553.55	1771,50	551.53	1223.17	593.61
T (K)	296(2)	293(2)	293(2)	293(2)	296(2)
Crystal system	trigonal	trigonal	monoclinic	triclinic	monoclinic
Space group	$P3(2)$	$P3(1)$	$P2_1/c$	$P\bar{1}$	$C2/c$
a (Å)	11.1272(3)	19.2466(5)	9.4120(3)	7.3679(3)	46.945(5)
b (Å)	11.1272(3)	19.2466(5)	6.5791(2)	10.5031(4)	4.462(5)
c (Å)	10.5243(4)	11.2555(3)	22.4300(8)	22.0348(9)	16.246(5)
α (°)	90	90	90	81.661(2)	90
β (°)	90	90	94.428(2)	88.311(2)	95.795(5)
γ (°)	120	120	90	73.326(2)	90
V (Å^3)	1128.48(6)	3610.80(16)	1384.78(8)	1616.08(11)	3386(4)
Z, ρ_{calc} (g cm^{-3})	3, 2.444	3, 2.444	4, 2.645	2, 2.514	8, 2.329
μ (mm^{-1})	12.383	11.721	13.454	11.551	11.015
F(000)	756	2430	1000	1128	2192
Crystal size (mm)	0.16 × 0.15 × 0.13	0.316 × 0.081 × 0.076	0.322 × 0.088 × 0.049	0.345 × 0.046 × 0.038	0.3 × 0.03 × 0.03
θ range (°)	2.11–27.15	1.22–26.77	1.82–27.13	0.93–29.67	2.52–30.47
Limiting indices (h, k, l)	$-14 \leqslant h \leqslant 14$ $-14 \leqslant k \leqslant 14$ $-13 \leqslant l \leqslant 13$	$-24 \leqslant h \leqslant 24$ $-24 \leqslant k \leqslant 24$ $-13 \leqslant l \leqslant 14$	$-11 \leqslant h \leqslant 11$ $-8 \leqslant k \leqslant 8$ $-28 \leqslant l \leqslant 28$	$-10 \leqslant h \leqslant 10$ $-14 \leqslant k \leqslant 14$ $-30 \leqslant l \leqslant 30$	$-66 \leqslant h \leqslant 65$ $-6 \leqslant k \leqslant 6$ $-22 \leqslant l \leqslant 23$
Reflections collected	7877	39 885	18 831	48 330	28 446
Reflections unique	2988	8475	3031	9112	5159
Completeness to θ_{max} (%)	92.9	90.0	98.9	99.5	99.8
Absorption correction	Gaussian	Gaussian	Gaussian	Gaussian	semi-emp. from equivls.
Minimum and maximum transmission	0.2420 and 0.2959	0.1480 and 0.4943	0.6839 and 0.9716	0.7272 and 1.0000	1 and 0.9067
Data/restraints/parameters	2988/1/146	8475/2/356	3031/0/145	9112/0/361	5159/0/172
Goodness-of-fit on F^2	1.119	0.905	1.005	0.979	0.997
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0673$, $wR_2 = 0.1467$	$R_1 = 0.0573$, $wR_2 = 0.1248$	$R_1 = 0.0223$, $wR_2 = 0.0361$	$R_1 = 0.0350$, $wR_2 = 0.0475$	$R_1 = 0.0332$, $wR_2 = 0.0587$
R indices (all data)	$R_1 = 0.0798$, $wR_2 = 0.1510$	$R_1 = 0.0909$, $wR_2 = 0.1340$	$R_1 = 0.0396$, $wR_2 = 0.0404$	$R_1 = 0.0806$, $wR_2 = 0.0569$	$R_1 = 0.0732$, $wR_2 = 0.0689$
Largest difference in peak and hole (e Å^{-3})	3.623 and −2.068	2.790 and −1.377	0.866 and −0.625	0.832 and −0.926	1.231 and −0.961

Table 2
Crystallographic data and refinement parameters for **6** and **7**.

	6	**7**
Empirical formula	$C_{13}H_{17}NO_2S_2Hg$	$C_{14}H_{19}NS_2Hg$
Fw (g mol^{-1})	483.99	466.01
T (K)	296(2)	293(2)
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_12_12_1$
a (Å)	11.6298(5)	7.269(5)
b (Å)	8.6838(4)	12.438(5)
c (Å)	14.9713(6)	16.896(5)
α (°)	90	90.000(5)
β (°)	92.504(2)	90.000(5)
γ (°)	90	90.000(5)
V (Å^3)	1510.52(11)	1527.6(13)
Z, ρ_{calc} (g cm^{-3})	4, 2.128	4, 2.026
μ (mm^{-1})	10.462	10.332
F(000)	920	888
Crystal size (mm)	0.16 × 0.10 × 0.08	0.716 × 0.057 × 0.05
θ range (°)	1.75–29.65	2.03–27.22
Limiting indices (h, k, l)	$-16 \leqslant h \leqslant 16$ $-12 \leqslant k \leqslant 12$ $-20 \leqslant l \leqslant 20$	$-9 \leqslant h \leqslant 8$ $-15 \leqslant k \leqslant 15$ $-21 \leqslant l \leqslant 21$
Reflections collected	43 937	12 084
Reflections unique	4250	3260
Completeness to θ_{max} (%)	99.7	97.8
Absorption correction	Gaussian	Gaussian
Minimum and maximum transmission	0.2853 and 0.4882	0.1346 and 0.6645
Data/restraints/parameters	4250/0/173	3260/0/164
Goodness-of-fit on F^2	1.015	0.995
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0253$, $wR_2 = 0.0441$	$R_1 = 0.0282$, $wR_2 = 0.0515$
R indices (all data)	$R_1 = 0.0475$, $wR_2 = 0.0499$	$R_1 = 0.0424$, $wR_2 = 0.0552$
Largest difference in peak and hole (e Å^{-3})	0.489 and −0.664	0.553 and −0.515

formed. Yellow crystals of the product were obtained from the solution after 7 days stored. Yield: 62% based on Hg{Te(dmb)}$_2$.

Properties: Air stable, yellow crystalline substance. Melting point: 151–153 °C. *Anal.* Calc. for $C_{26}H_{34}Hg_2N_2O_4S_4Te_2$ (1223.17): C, 25.53; H, 2.80, N, 2.29. Found: C, 25.51; H, 2.85; N, 2.24%. IR (KBr): 3010 [ν_s(C–H)]; 2952 [ν_s(C–H)]; 1582 [ν_s(C=C)]; 1241 [ν_s(C–N)]; 1167 [ν_s(C=S)]; 1103 [ν_{as}(C–O–C)]; 998 [δ_{ip}(C=C–H)]; 946 [ν_s(C–S)]; 749 [δ_{op}(C=C–H)], 450 cm^{-1} [δ_{op}(C=C–C)].

*2.6. Preparation of [Hg{Te(mes)($S_2CNC_4H_8$)}]$_n$ (**5**)*

To 0.069 g (0.1 mmol) of Hg{Te(mes)}$_2$ dissolved in 6 mL of DMSO, 0.017 g (0.1 mmol) of sodium pyrrolidine dithiocarbamate were added. After 1 h stirring at 40 °C a yellow solution was formed. Yellow crystals of the product were obtained after 7 days laying up of the solution. Yield: 82% based on Hg{Te(mes)}$_2$.

Properties: Air stable, yellow crystalline substance. Melting point: 169–171 °C. *Anal.* Calc. for $C_{14}H_{19}HgNS_2Te$ (593.61): C, 28.33; H, 3.23; N, 2.36. Found: C, 28.48; H, 3.30; N, 2.34%. IR (KBr): 3000 [ν_s(C–H)]; 2962 [ν_s(C–H)]; 1444 [ν_s(C=C)]; 1292 [ν_s(C–N)]; 1165 [ν_s(C=S)]; 1025 [δ_{ip}(C=C–H)]; 946 [ν_s(C–S)]; 844 [δ_{op}(C=C–H)], 450 cm^{-1} [δ_{op}(C=C–C)].

*2.7. Preparation of [Hg(dmb)($S_2CNC_4H_8$)] (**6**)*

To 0.073 g (0.1 mmol) of Hg{Te(dmb)}$_2$ dissolved in 6 mL of DMSO, 0.017 g (0.1 mmol) of sodium pyrrolidine dithiocarbamate were added. After 24 h stirring at 40 °C a yellow, cloudy solution was formed. The colorless main crystals isolated were obtained over the course of 10 days, corresponding to 6. Yield: 73% based on sodium pyrrolidine dithiocarbamate.

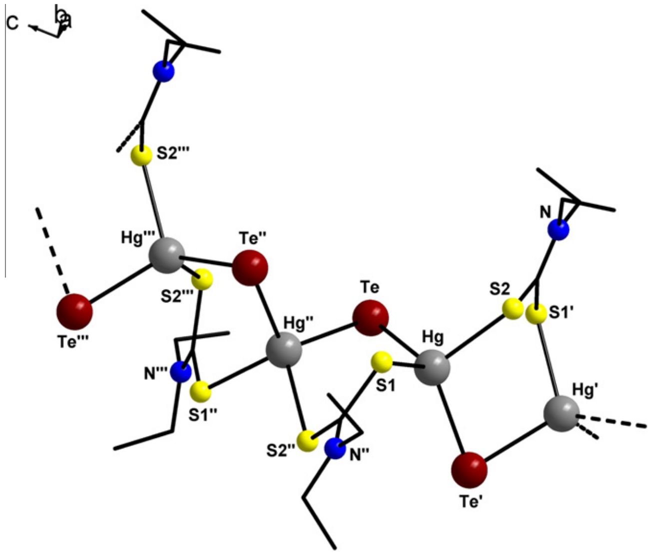


Fig. 1. The polymeric structure and the screw-shaped configuration of the Hg and Te atoms of [Hg(TePh)(S$_2$CNEt$_2$)]$_n$ (**1**). For clarity, the phenyl groups bound to the tellurium atoms, as well as the hydrogen atoms are not shown. Symmetry transformations used to generate equivalent atoms: (′) = 1 − *y*, −1 + *x* − *y*, −0.33333 + *z*; (″) = 2 − *x* + *y*, 1 − *x*, 0.33333 + *z*; (‴) = 1 − *y*, −1 + *x* − *y*, 0.66667 + *z*.

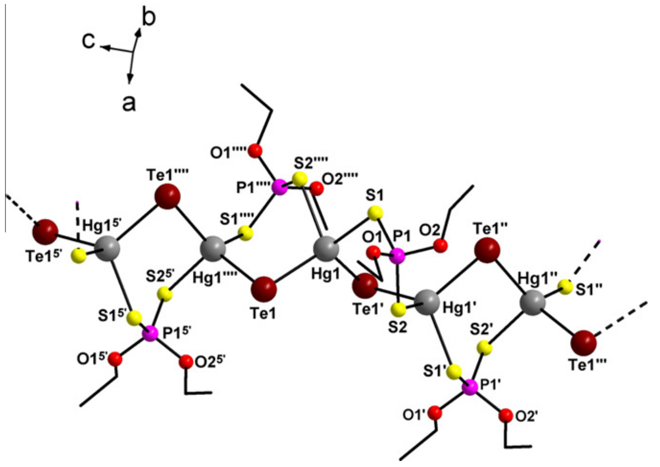


Fig. 2. The polymeric structure and the helical organization of mercury and tellurium of [Hg(TePh){S$_2$P(OEt)$_2$}]$_n$ (**2**). For clarity, the phenyl groups bound to the Te atoms, as well as the hydrogen atoms are not shown. Symmetry transformations used to generate equivalent atoms: (′) = 4 − *x* + *y*, 2 − *x*, −0.33333 + *z*; (″) = 2 − *y*, −2 + *x* − *y*, −66667 + *z*; (‴) = *x*, *y*, 1 − *z*; (⁗) = 2 − *y*, −2 + *x* − *y*, 0.33333 + *z*; (″‴) = 4 − *x* + *y*, 2 − *x*, 0.66667 + *z*.

Properties: Air stable, colorless crystalline substance. Melting point: 159–161 °C. *Anal.* Calc. for $C_{13}H_{17}NO_2S_2Hg$ (483.99): C, 38.00; H, 4.17; N, 3.41. Found: C, 39.45; H, 4.24; N, 3.34%. IR (KBr): 3100 [ν_s(C–H)]; 2970 [ν_s(C–H)]; 1582 [ν_s(C=C)]; 1237 [ν_s(C–N)]; 1161 [ν_s(C=S)]; 1102 [ν_{as}(C–O–C)]; 1000 [δ_{ip}(C=C–H)]; 946 [ν_s(C–S)]; 758 [δ_{op}(C=C–H)]; 455 cm^{-1} [δ_{op}(C=C–C)].

2.8. Preparation of [Hg(mes)($S_2CNC_4H_8$)] (7)

To 0.069 g (0.1 mmol) of Hg{Te(mes)}$_2$ dissolved in 6 mL of DMSO, 0.017 g (0.1 mmol) of sodium pyrrolidine dithiocarbamate were added. After 24 h stirring at 40 °C a yellow, cloudy solution was attained. The colorless main crystals isolated were obtained in the course of 15 days, corresponding to **7**. Yield: 64% based on sodium pyrrolidine dithiocarbamate.

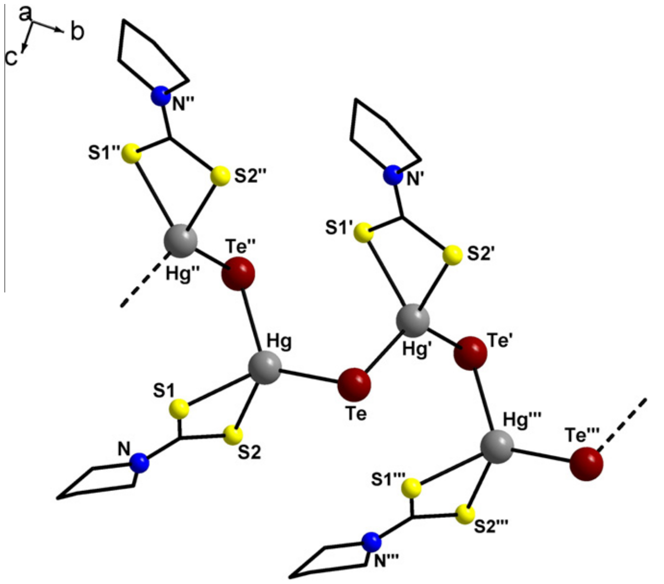


Fig. 3. The polymeric, screw-shaped structure of compound [Hg(TePh)(S$_2$CNC$_4$H$_8$)]$_n$ (**3**). For clarity, the phenyl groups bound to the Te atoms, as well as the hydrogen atoms are not shown. Symmetry transformations used to generate equivalent atoms: (′) = 1 − *x*, 0.5 + *y*, 0.5 − *z*; (″) = 1 − *x*, −0.5 + *y*, 0.5 − *z*; (‴) = *x*, 1 + *y*, *z*.

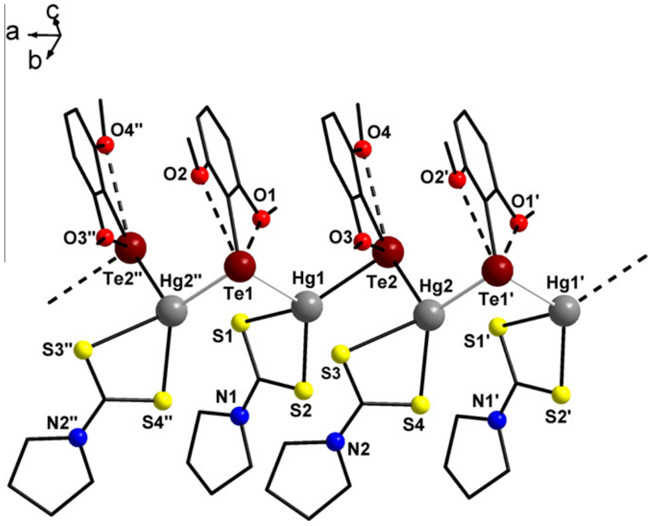


Fig. 4. The polymeric, zigzag structure of [Hg{Te(dmb)(S$_2$CNC$_4$H$_8$)}]$_n$ (**4**). For clarity, the hydrogen atoms are not shown. The dashed lines identify the Te–O secondary interactions. Symmetry transformations used to generate equivalent atoms: (′) = −1 + *x*, *y*, *z*; (″) = 1 + *x*, *y*, *z*.

Properties: Air stable, colorless crystalline substance. Melting point: 179–181 °C. *Anal.* Calc. for $C_{14}H_{19}NS_2Hg$ (466.01): C, 42.78; H, 4.87; N, 3.56. Found: C, 42.43; H, 5.02; N, 3.52. IR (KBr): 3100 [ν_s(C–H)]; 2954 [ν_s(C–H)]; 1568 [ν_s(C=C)]; 1249 [ν_s(C–N)]; 1166 [ν_s(C=S)]; 1028 [δ_{ip}(C=C–H)]; 947 [ν_s(C–S)]; 703 [δ_{op}(C=C–H)], 451 cm^{-1} [δ_{op}(C=C–C)].

2.9. X-ray structural determination

Data were collected with a Bruker APEX II CCD area-detector diffractometer and graphite-monochromatized Mo Kα radiation. The structures were solved by direct methods using SHELXS-97

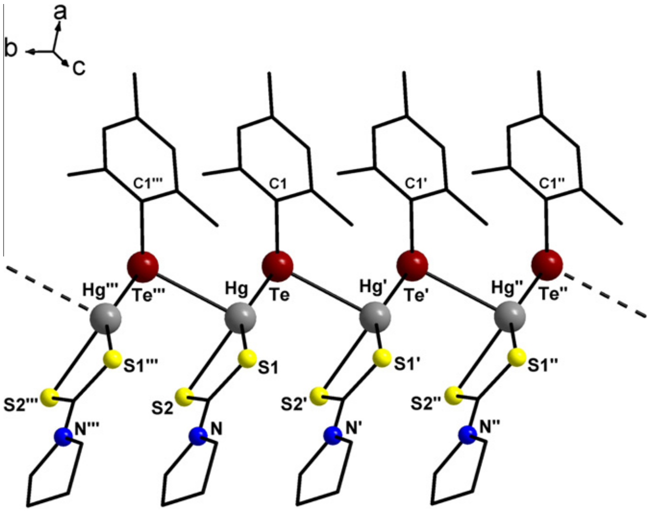


Fig. 5. The polymeric, zigzag structure of compound $[Hg\{Te(mes)(S_2CNC_4H_8)\}]_n$ (**5**). For clarity, the hydrogen atoms are not shown. Symmetry transformations used to generate equivalent atoms: (′) = *x*, −1 + *y*, *z*; (″) = *x*, −2 + *y*, *z*; (‴) = *x*, 1 + *y*, *z*.

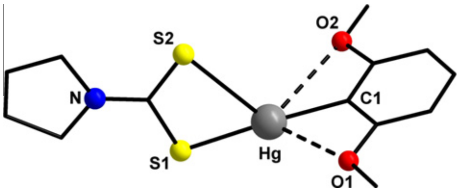


Fig. 6. Molecular structure of $[Hg(dmb)(S_2CNC_4H_8)]$ (**6**). Dashed lines are secondary interactions. For clarity, the hydrogen atoms are not shown.

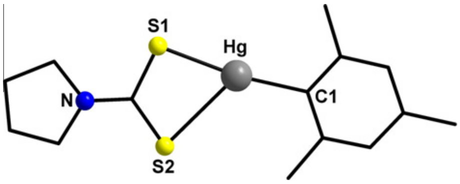


Fig. 7. Molecular structure of $[Hg(mes)(S_2CNC_4H_8)]$ (**7**). For clarity, the hydrogen atoms are not shown.

[13]. Subsequent Fourier-difference map analyses yielded the positions of the non-hydrogen atoms. Refinements were carried out with the SHELXL-97 package [13]. All refinements were made by full-matrix least-squares on F^2 with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were included in the refinement in calculated positions. Crystal data and more details of the data collections and refinements are contained in Tables 1 and 2.

3. Discussion

Figs. 1–5 show the polymeric structure of compounds **1**–**5**, and Figs. 6 and 7 display the mononuclear molecules of **6** and **7**. Table 3 resumes selected bond angles and lengths for the reactions products **1**–**7**.

The structures of compounds **1**, **2** and **3** are very similar, since these three polymers, although containing different dithio groups, show all a helical pattern of the bound Hg–Te atoms. While the tetrahedral configuration of the Hg atoms in **1** and **2** is attained

Table 3
Selected bond lengths (Å) and angles (°) for **1**–**7**.

Bond lengths		Bond angles	
1		**1**	
Te–Hg	2.7566(1)	Hg″–Te–Hg	83.980(1)
Te′–Hg	2.7755(1)	Te–Hg–Te′	112.423(1)
Hg–S1	2.6039(0)	Te–Hg–S1	109.633(1)
Hg–S2	2.5909(1)	Te–Hg–S2	113.933(1)
		S1–Hg–S2	93.490(1)
		Te′–Hg–S2	109.476(1)
		Te′–Hg–S1	116.640(1)
2		**2**	
Te1–Hg1	2.7441(16)	Hg1″″–Te1–Hg1	91.894(1)
Hg1–Te1′	2.7542(15)	Te1–Hg1–Te1′	114.401(1)
Hg1–S1	2.590(6)	Te1–Hg1–S1	122.624(1)
Hg1–S2″″	2.656(6)	Te1–Hg1–S2″″	106.350(1)
		S1–Hg1–S2″″	86.736(1)
		Te1′–Hg1–S2″″	113.527(1)
		Te1′–Hg1–S1	109.832(1)
3		**3**	
Te–Hg	2.7069(1)	Te–Hg–Te″	123.720(1)
Te–Hg′	2.7879(1)	Te–Hg–S1	121.915(1)
Hg–S1	2.6375(1)	Te–Hg–S2	118.485(1)
Hg–S2	2.6114(1)	Te″–Hg–S1	105.768(1)
		Te″–Hg–S2	104.347(1)
		S1–Hg–S2	69.386(1)
		Hg–Te–Hg′	96.419(1)
4		**4**	
Te1–Hg1	2.8008(1)	Hg2″–Te1–Hg1	86.64(2)
Te1–Hg2″	2.7387(1)	Hg2″–Te1···O1	80.302(2)
Te2–Hg2	2.7998(1)	Hg2″–Te1···O2	110.991(2)
Te2–Hg1	2.7413(1)	Hg1–Te1···O1	59.166(1)
Hg1–S1	3.0263(1)	Hg1–Te1···O2	147.678(2)
Hg1–S2	2.5170(1)	Hg1–Te2–Hg2	87.871(2)
Hg2–S3	2.9251(1)	Hg1–Te2···O3	80.108(2)
Hg2–S4	2.5426(1)	Hg1–Te2···O4	110.009(2)
Te1···O1	3.1888(1)	Hg2–Te2···O3	60.661(1)
Te1···O2	3.0904(1)	Hg2–Te2···O4	148.584(2)
Te2···O3	3.2075(1)	Te1–Hg1–Te2	110.822(2)
Te2···O4	3.0708(1)	S1–Hg1–S2	64.033(2)
		Te1–Hg1–S1	97.645(2)
		Te1–Hg1–S2	124.927(2)
		Te2–Hg1–S1	124.215(2)
		Te2–Hg1–S2	122.524(2)
		Te2–Hg2–Te1′	111.265(2)
		S3–Hg2–S4	65.318(2)
		Te2–Hg2–S3	97.883(2)
		Te2–Hg2–S4	121.317(2)
		Te1′–Hg2–S3	123.692(2)
		Te1′–Hg2–S4	125.019(2)
5		**5**	
Hg–Te	2.6241(16)	Hg–Te–Hg′	101.30(6)
Te′–Hg′	3.131(2)	Te‴–Hg–S1	82.53(5)
Hg–S1	2.7293(15)	Te‴–Hg–S2	98.88(6)
Hg–S2	2.4841(16)	Te–Hg–S1	134.15(3)
Te–C1	2.131(5)	Te–Hg–S2	150.49(3)
		S2–Hg–S1	69.69(4)
6		**6**	
Hg–C1	2.0596(4)	S2–Hg–C1	117.430(2)
Hg···O2	3.0615(3)	S1–Hg–C1	175.396(2)
Hg···O1	3.0698(1)	S1–Hg···O2	129.007(2)
Hg–S1	2.3731(2)	S1– Hg···O1	131.623(1)
Hg–S2	2.9611(1)	S2–Hg···O1	110.703(3)
		S2–Hg···O2	103.966(4)
		S1–Hg–S2	66.970(3)
		O1···Hg···O2	99.087(1)
7		**7**	
Hg–C1	2.0646(8)	S1–Hg–C1	171.594(26)
Hg–S1	2.397(1)	S2–Hg–C1	121.428(14)
Hg–S2	2.9208(8)	S1–Hg–S2	66.97(1)
Hg···C7	3.2168(8)	S2– Hg···C7	170.68(1)
Hg···C9	3.2898(9)	S2–Hg···C9	71.16(1)

(*continued on next page*)

Table 3 (*continued*)

Bond lengths	Bond angles	
	S1–Hg···C9	137.743(19)
	S1–Hg···C7	120.405(13)
	C7···Hg···C9	101.835(8)

Symmetry transformations used to generate equivalent atoms: **1**: (′) = 1 − *y*, −1 + *x* − *y*, −0.33333 + *z*; (″) = 2 − *x* + *y*, 1 − *x*, 0.33333 + *z*. **2**: (′) = 4 − *x* + *y*, 2 − *x*, −0.3333 + *z*; (″″) = 2 − *y*, −2 + *x* − *y*, 0.3333 + *z*. **3**: (′) = 1 − *x*, 0.5 + *y*, 0.5 − *z*; (″) = 1 − *x*, −0.5 + *y*, 0.5 − *z*. **4**: (′) = −1 + *x*, *y*, *z*; (″) = 1 + *x*, *y*, *z*. **5**: (′) = *x*, −1 + *y*, *z*; (‴) = *x*, 1 + *y*, *z*.

by two sulfur atoms assigned to two dithio groups, in compound **3** (and also in **4**, **5**, **6** and **7**) single dithio groups provide two sulfurs atoms for each Hg, allowing the metal atoms maintain their tetrahedral arrangement. The sulfur atoms of the ligands dedtc, dedtp and pyrrolidine dithiocarbamate can act as bridge-forming or bidentate ligands. Factors influencing either function are: the conditions of the reaction, the presence of co-ligands and the stereochemistry of the end products. These effects are also observable with the dithio ligand $R_2N–CS_2$ [14] and with the thio ligand 4,6-dimethyl-2-pyrimidinethiolate [15]. In compounds **1**, **2** and **3** the medium distances Hg–S1/Hg–S2 are respectively 2.6105 and 2.6194 Å, but, on the contrary, the Hg–S1/Hg–S2 bonds in **4**, **5**, **6** and **7** are very asymmetrical (see Table 3).

While in the polymers **1**, **2** and **3** the Hg–Te distances are around 2.75 Å, in the zigzag configured compound **4** the Te1(Te2)–Hg1 distances reach 2.8008 Å, whereas the Te1(Te2)–Hg2 bonds retain the "normal" distances, approximately 2.735 Å. In the also zigzag configured polymer **5** the asymmetry of the Hg–Te distances achieve the maximum values: 2.6242 (Hg–Te) and 3.1350 Å (Hg–Te′). As the sum of the Hg/Te van der Waals radii is 3.61 Å, the Hg–Te′ interactions can be considered as effective bonds.

The polymeric structures of compounds **1**–**5** are not observed in the complexes $[Hg(dmb)(S_2CNC_4H_8)]$ (**6**) and $[Hg(mes)(S_2CNC_4H_8)]$ (**7**). Since these two compounds were prepared by extended stirring at 40 °C of the mother solutions of **4** and **5**, respectively, they (**6** and **7**) are supposed to be decomposition products of polymers **4** and **5**. It is not wrong to assert that, at the end of the reactions, only the products (**6** and **7**), starting materials $\{Hg(mesTe)_2$, $Hg(dmbTe)_2\}$ and the side products $(mesTe)_2$ and $(dmbTe)_2$ were present [1].

In the species **6** and **7** the Hg atoms show its typical (mainly) linear bonds, S1–Hg–C1 {175.396(2)°, **6** and 171.594(26)°, **7**}. Such linear bonds are not observable when Te is one of the terminal atoms, as shown by the compounds **1**–**5**.

Acknowledgments

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Appendix A. Supplementary data

CCDC 900906–900912 contain the supplementary crystallographic data for **1**–**7**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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