Syntheses and Structures of New Tellurium−Mercury Clusters with Twelve- and Six-Membered Rings

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Clusters with polycyclic twelve-membered rings were formed exclusively from the reaction of $[Hg(TePh)_2]$ with HgX_2 in pyridine. Clusters with just six members were formed from the same reaction in DMSO. In both cases, the solvent was coordinated to the clusters. The clusters, $[Hg_6(\mu\text{-}Br)_2Br_2(\mu\text{-}TePh)_8(py)_2]$ and $[Hg_3X_3(\mu\text{-}TePh)_3]\cdot 2DMSO$ (X = Cl, Br, I), were characterized by single-crystal X-ray crystallography.

Mercury chalcogenide compounds have found considerable use in industry, especially as low band gap semiconductors, in photovoltaic applications, and IR detection devices.[1] The synthesis and structural characterization of metal chalcogenide molecules with a defined size and structure provide an interesting approach to this class of materials.[2] Coordination compounds can be adequate precursors because the structure and properties of the resulting material can be modified by the synthesis conditions or the nature and properties of the ligands. Diorganochalcogenide compounds, RE−ER (E = S, Se, Te), could be optimal ligands, because they react with mercury under mild conditions to yield $[Hg(ER)_2]$ complexes. Although they eventually form polymeric structures by weak intermolecular Hg···E interactions,[3,4] the sulfide and selenide derivatives react with equimolar amounts of $HgCl_2$ in pyridine to yield metallacyclic compounds $[Hg_4Cl_4(\mu\text{-}ER)_4(py)_n]$ (E = S, R = *t*Bu, $n = 2$;[5] E = Se, R = Et, $n = 4$; E = Se, R = *t*Bu, $n = 4$.[3]) The different stoichiometry of the compounds appears to depend on the steric hindrance between pyridine and organic substituent R. Surprisingly, analogous tellurium derivatives have not been reported until now. As part of our interest in organotelluride chemistry,[6] we have investigated the reaction of $[Hg(TePh)_2]$[7] with $HgBr_2$ in coordinating solvents, in which only the first is soluble.

The solid isolated from the reaction mixture could be fully characterized as the cluster $[Hg_6(\mu\text{-}Br_2)Br_2(\mu\text{-}TePh)_8(py)_2]$ (**1**) by single-crystal X-ray diffraction[8] (Figure 1). The structure of **1** exemplifies a rare multinuclear compound. The molecule can be considered as being formed from two six-membered $Hg_3(\mu{-}TePh)_3$ rings that are bridged by two (μ-TePh) ligands. Additionally, a bromine atom asymmetrically bridges the two mercury atoms in each ring [Hg(1)−Br(8) 2.941(2), Hg(3)−Br(8) 2.845(2) Å]. A terminal bromine atom coordinates to the third mercury atom at a shorter distance [Hg(2)−Br(9) 2.641(2) Å].

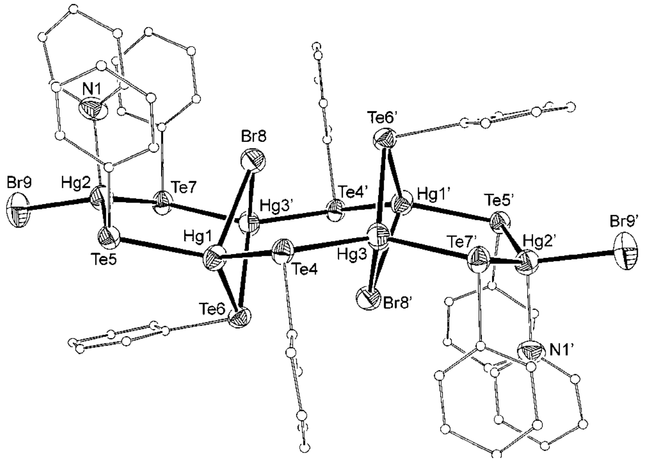

Figure 1. Structure of **1** (with H atoms omitted and each carbon atom represented by a conventional radius for clarity); selected bond lengths [Å]: Hg(1)−Te(4) 2.7489(13), Hg(1)−Te(6) 2.7552(15), Hg(1)−Te(5) 2.7796(13), Hg(1)−Br(8) 2.941(2), Hg(2)−N(1) 2.421(19), Hg(2)−Br(9) 2.641(2), Hg(2)−Te(5) 2.7432(13), Hg(2)−Te(7) 2.7568(15), Hg(3)−Te(7)′ 2.7511(13), Hg(3)−Te(4) 2.7564(13), Hg(3)−Br(8)′ 2.845(2), Hg(3)−Te(6)′ 2.8500(15), Te(6)−Hg(3)′ 2.8501(15), Te(7)−Hg(3)′ 2.7511(13); ′ = $-x + 1, -y, -z + 1$

The structure of **1** resembles those found of $[Et_4N]_4[Hg_7(\mu\text{-}Se)_6(\mu\text{-}Se_2)(\mu_3\text{-}Se)_2]$[9a] (Figure 2A) and $[nBu_4N]_4[Hg_4(\mu\text{-}Te)_2(\mu\text{-}Te_2)_2(\mu\text{-}Te_3)_2]$[9b] (Figure 2B), both of which contain only two coordinated chalcogen atoms. In these anionic clusters, two Hg_3Se_3 or $Hg_2(Te_3)Te$ rings are

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bridged by Se^{2-}, Se_2^{2-}, and $HgSe_2^{2-}$, or Te_2^{2-} and Te^{2-} units. The Hg−Hg distances in **1** [Hg(1)−Hg(3) = 3.6249(11) Å is the shortest] preclude a metal−metal interaction.

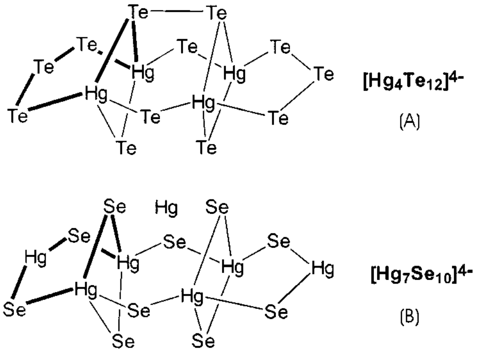

Figure 2. Structures of the clusters $[Hg_7(\mu\text{-}Se)_6(\mu\text{-}Se_2)(\mu_3\text{-}Se)_2]^{4-}$ [9a] (A) and $[Hg_4(\mu\text{-}Te)_2(\mu\text{-}Te_2)_2(\mu\text{-}Te_3)_2]^{4-}$ [9b] (B)

Although the coordination geometry around all the mercury atoms in **1** is a distorted tetrahedron, two different environments coexist about the atoms: $HgBrTe_3$ [for Hg(1) and Hg(3)] and $HgBrTe_2N$ [for Hg(2)]. No compounds with the same environment around the three-coordinate Te atom (two Hg atoms and an alkyl or aryl group) have been reported in the Cambridge Crystallographic Database.[10] However, the Hg−Te bond lengths [2.7423(13)−2.8500(15) Å] are similar to those found in other mercury(II) tellurides containing two-coordinate Te atoms (two Hg atoms)[9b,13] or three-coordinate with two Hg atoms and one P atom.[12] The only other reported Hg−Te distances for three-coordinate Te (two Hg atoms and a Te atom) are much longer.[9a,9b] The Hg−Br and Hg−N distances are normal.[13] All the Te atoms are trigonal-pyramidal with each bonding to two Hg atoms and a carbon atom of the phenyl group [bond angles ranging between Hg(1)−Te(6)−Hg(3) 80.57(4)° and C(71)−Te(7)−Hg(3)′ 104.6(5)°; ′ = $-x + 1$, $-y$, $-z + 1$].

Compound **1** is sparingly soluble in most organic solvents except pyridine, DMSO, and DMF. Furthermore, **1** is a very stable compound and was the main product formed when mixtures of $[Hg(TePh)_2]$ and $HgBr_2$ and an excess of other ligand (for instance PPh_3) in pyridine were allowed to crystallize. On the other hand, all attempts to substitute pyridine for another ligand were unsuccessful.

The reaction of $[Hg(TePh)_2]$ and $HgBr_2$ in DMSO yielded a crystalline light yellow solid (**2a**), whose composition was determined by single-crystal X-ray diffraction as $[Hg_3Br_3(TePh)_3]\cdot 2DMSO$.[13] The molecular structure of **2a** (Figure 3) consists of a six-membered ring with alternating Hg and Te atoms in a chair conformation. Although a similar conformation is observed as for **1**, in this case the orientation of all phenyl groups of the TePh ligands are on the same side of the ring (in **1**, two groups occupy one side and one group occupies the other). A terminal bromine atom coordinates to each mercury atom. The Hg−Te and Hg−Br distances are similar to the corresponding distances observed in **1**. If we consider only the interactions noted above, the coordination geometry around the mercury atom would be trigonal-planar. However, two DMSO molecules (one of them crystallographically disordered about two positions) occupy positions on either side of the Hg_3Te_3 ring with the oxygen atoms directed to the center of the ring. The distance of O(21) to the mercury atoms is shorter than that of O(11) [Hg(1)−O(21) 3.176(11), Hg(2)−O(21) 2.832(9), Hg(3)−O(21) 2.908(9), Hg(1)−O(11) 3.2380(15), Hg(2)−O(11) 3.344(9) and Hg(3)−O(11) 3.346(8) Å]. Atom O(21) seems to establish a weak interaction with the tellurium atoms; the Te···O(21) distances range between 3.161(8) and 3.252(9) Å. Each mercury atom also interacts weakly with the bromine atoms of the neighboring molecules [Hg(1)···Br(1)′ = 3.2380(15), Hg(2)···Br(2)′′ = 3.4881(15) and Hg(3)···Br(3)′′′ = 3.4640(16) Å; ′ = $x + 1$, $-y + 1$, $-z$; ′′ = $-x + 1$, $-y + 1$, $-z + 1$; ′′′ = $-x + 1$, $-y$, $-z + 1$]. If all weak interactions are considered, the resulting coordination polyhedron around the mercury atom can be described as a strongly distorted octahedron, while the co-

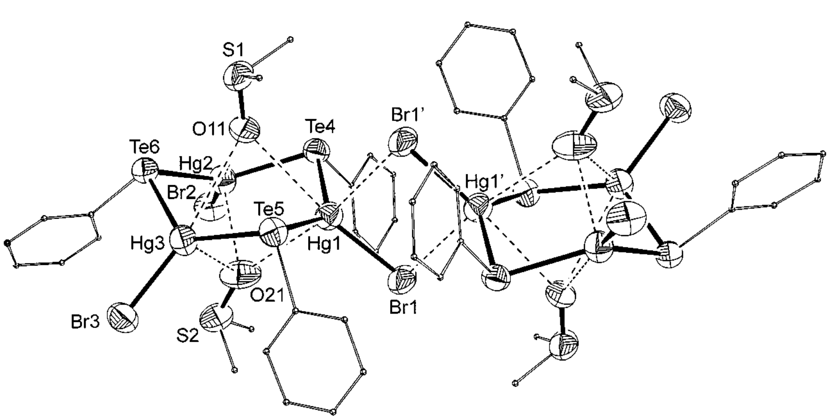

Figure 3. Two molecules of **2a**, showing intermolecular interactions (H atoms are omitted and each carbon atom represented by a conventional radius for clarity); selected bond lengths [Å]: Hg(1)−Br(1) 2.6134(13), Hg(1)−Te(4) 2.6884(9), Hg(1)−Te(5) 2.6974(9), Hg(2)−Br(2) 2.5859(15), Hg(2)−Te(6) 2.6855(9), Hg(2)−Te(4) 2.7139(9), Hg(3)−Br(3) 2.5824(13), Hg(3)−Te(5) 2.6929(9), Hg(3)−Te(6) 2.7062(9), Hg(1)−Br(1)′ 3.2380(15); ′ = $-x + 1, -y + 1, -z$

ordination geometry about the tellurium atoms is trigonal-pyramidal with the Hg−Te−Hg angles approximately 90°.

As compound **1** comprises $Hg_3(\mu\text{-}TePh)_3$ units, **2a** therefore could be considered to be its structural precursor. An interesting aspect is that changing the reaction solvent affects the stoichiometry as well as the structure of the resulting compound. Furthermore, the DMSO molecules in **2a** seem to shield the mercury atoms, but they are not strongly bonded to them. The compounds $[Hg_3Cl_3(\mu\text{-}TePh)_3]\cdot 2DMSO$ (**2b**) and $[Hg_3I_3(\mu\text{-}TePh)_3]\cdot 2DMSO$ (**2c**), which are isostructural with analogs **2a**, were also characterized. Studies to evaluate the stoichiometry and structure of the products from the reaction of **2** with other ligands in different solvents are underway in our laboratory.

Experimental Section

$(PhTe)_2Hg$ (0.61 g, 1.0 mmol) was dissolved in 10 mL of dry pyridine for **1** or DMSO for **2a**, and subsequently $HgBr_2$ (0.36 g, 1 mmol) was added under dry N_2. After stirring for 4 h at room temperature, the yellow solution was filtered. The addition of ethanol (2 mL) produced yellow crystals after a week (**1**: 0.497 g, 60% yield based on $HgBr_2$, m.p. 104 °C; **2a**: 0.172 g, 32% yield based on $HgBr_2$, m.p. 118 °C; **2b**: 0.223 g, 45% yield based on $HgCl_2$, m.p. 106−107 °C; **2c**: 0.263 g, 45% yield based on HgI_2, m.p. 125−126 °C).

Acknowledgments

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[8] Crystal data for **1**: $C_{58}H_{50}Br_4Hg_6N_2Te_8$, triclinic, $P\bar{1}$ (no. 2), a = 12.1079(7), b = 12.2316(7), c = 15.6690(9) Å, α = 69.6370(10), β = 67.5350(10), γ = 63.1920(10)°, V = 1870.09(19) Å^3, Z = 2, Mo-K_α (λ = 0.71073 Å), 8655 unique reflections (R_{int} = 0.1305). Final residuals R_1 = 0.0760 and wR_2 = 0.1937 [$I > 2\sigma(I)$], 287 parameters, as supplementary publication no. CCDC-164994.

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[13] Crystal data for **2a**: $C_{22}H_{27}Br_3Hg_3O_2S_2Te_3$, triclinic, $P\bar{1}$ (no. 2), a = 10.2766(11), b = 14.1892(15), c = 14.5784(15) Å, α = 62.235(2), β = 72.606(2), γ = 89.866(2)°, V = 1771.3(3) Å^3, Z = 2, Mo-K_α (λ = 0.71073 Å), 10380 unique reflections (R_{int} = 0.0468). Final residuals R_1= 0.0419 and wR_2 = 0.0833 [$I > 2\sigma(I)$], 326 parameters, supplementary publication no. CCDC-164992. Crystal data for **2b**: $C_{22}H_{27}Cl_3Hg_3O_2S_2Te_3$, triclinic, $P\bar{1}$ (no. 2), a = 11.1468(9), b = 12.2189(10), c = 14.1336(11) Å, α = 107.2810(10), β = 107.752(2), γ = 100.832(2)°, V = 1666.5(2) Å^3, Z = 2, Mo-K_α (λ = 0.71073 Å), 10206 unique reflections (R_{int} = 0.0403). Final residuals R_1 = 0.0518 and wR_2 = 0.1260 [$I > 2\sigma(I)$], 316 parameters, supplementary publication no. CCDC-164991. Crystal data for **2c**: $C_{22}H_{27}Hg_3I_3O_2S_2Te_3$, triclinic, $P\bar{1}$ (no. 2), a = 11.1372(9), b = 12.4649(10), c = 15.4378(12) Å, α = 111.868(2), β = 102.381(2), γ = 102.1630(10)°, V = 1840.2(3) Å^3, Z = 2, Mo-K_α (λ = 0.71073 Å), 10874 unique reflections (R_{int}= 0.1094). Final residuals R_1 = 0.0676 and wR_2 = 0.1602 [$I > 2\sigma(I)$], 304 parameters, supplementary publication no. CCDC-164993. Crystallographic data (excluding structure factors) for the structures have been deposited with the Cambridge Crystallographic Data Center. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk], citing the supplementary publication numbers above.

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