Inorg. Chem. **2007**, *46*, 2356–2358

Inorganic Chemistry

Communication

Mercury Bis(phenyltellurolate) as a Precursor for the Synthesis of Binary and Ternary Nanoclusters

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Received January 2, 2007

The reaction of Hg(TePh)$_2$ with AgX (X = Cl, NO$_3$) in the presence of PPh$_3$ and PMePh$_2$ in dimethylformamide (DMF) affords the cluster [Hg$_6$Ag$_4$(TePh)$_{16}$] (**1**) at room temperature or [Hg$_6$Ag$_4$Te(TePh)$_{14}$]$_2$ (**2**) with heating. When Hg(TePh)$_2$ is reacted with [Co(PPh$_3$)$_2$Cl$_2$] or [Ni(PPh$_3$)$_2$Cl$_2$], the clusters [Hg$_8$Te(PhTe)$_{12}$Cl$_4$]Q [**3**; Q = [Co(DMF)$_6$]$^{2+}$ (**3a**), [Ni(DMF)$_6$]$^{2+}$ (**3b**)] are formed. The syntheses of **1** and **2** occur with the incorporation of Ag^{I} into the cluster, and the single-crystal analyses show that the two ternary clusters consist of Hg, Ag, and Te centers occupying well-defined positions. Compounds **3a** and **3b** do not show the incorporation of the metal into the cluster, but the Co^{II} and Ni^{II} salts provide the Cl atom to generate the anionic cluster **3** stabilized by the [Co(DMF)$_6$]$^{2+}$ or [Ni(DMF)$_6$]$^{2+}$ ion.

Ternary nanoclusters find widespread application in optical and electronic devices, justifying the development of a new general molecular synthetic route to access this material type.[1] There are relatively few reports on the preparation of ternary II−II′−VI nanomaterials. To date the exploration of binary metal telluride (MTe) nanoclusters[2] has been much more extensive in contrast to ternary (MM′Te) nanoclusters.[3] Corrigan and co-workers[2,3] attribute this, in part, to a lack of suitable "binary" silyl reagents that can be employed to yield ternary clusters.

Hg(EPh)$_2$ (E = Se, Te), an efficient delivery source of {ME} for the synthesis of binary clusters, forms polymeric structures by weak intermolecular Hg···E interactions in the solid state.[4,5] This class of compounds has been used previously in the synthesis of binary clusters, acting as templates to generate new compounds. For example, the sulfide and selenide derivatives react with equimolar amounts of HgCl$_2$ in pyridine to yield the metallacyclic compounds [Hg$_4$Cl$_4$(μ-ER)$_4$(py)$_n$] (E = S, R = ^{t}Bu, n = 2;[6] E = Se, R = Et, n = 4; E = Se, R = ^{t}Bu, n = 4[4]). The different stoichiometries of the compounds appear to depend on the steric hindrance between pyridine and the organic substituents R.

As part of our interest in organochalcogenide chemistry,[7] we have investigated the reaction of Hg(EPh)$_2$ with HgX$_2$ (E = Se, Te; X = Cl, Br, I) in coordinating solvents,[8] the only way to solubilize Hg(EPh)$_2$. The reaction of Hg(EPh)$_2$ with HgX$_2$ in dimethyl sulfoxide (DMSO) yields a cluster with the general formula [Hg$_3$X$_3$(EPh)$_3$]·2DMSO. The molecular structure of this cluster is a six-membered ring with alternating Hg and chalcogen atoms in a chair conformation. The larger cluster [Hg$_6$(μ-Br$_2$)Br$_2$(μ-TePh)$_8$(py)$_2$] is produced from the same reagents, Hg(TePh)$_2$ with HgBr$_2$, in pyridine. The molecule can be considered as formed from two six-

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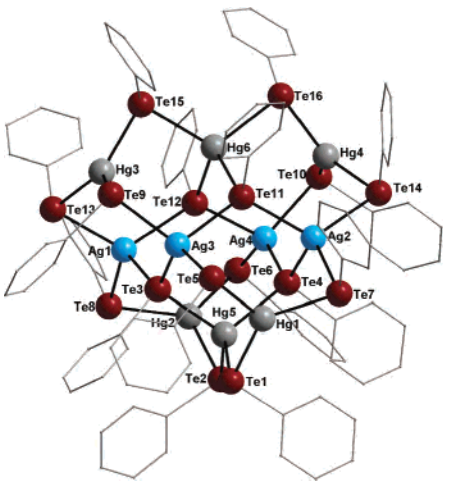

Figure 1. Structure of **1** (the H atoms are omitted, and the C atoms are represented as sticks for clarity).

membered rings $Hg_3(\mu\text{-}TePh)_3$, which are bridged by two (μ-TePh) ligands. In order to verify the steric requirements of the organic residues of the telluride building blocks, we have attempted a reaction between $Hg(n\text{-}C_3H_7Te)_2$ and $HgBr_2$ in DMSO.[9] When the same synthetic procedure as that previously used is applied, the cluster $[Hg_8(\mu\text{-}n\text{-}C_3H_7Te)_{12}(\mu\text{-}Br)Br_3]$ is obtained. Studies on the reactivity of these Hg clusters, as well as attempts to open the HgTe rings, are, in general, restricted because of the clusters' remarkably low solubility. To investigate the possibility of formation of the unstable solvent-coordinated intermediary PhTeHgX, we have recently reported the reaction of $[Hg_3Cl_3(TePh)_3]\cdot 2DMSO$ with $Co[Hg(SCN)_4]$ in DMSO, where the polymeric complex $[Co(DMSO)_2(NCS)_4(HgTePh)_2]_n$ is produced,[10] an example of the chemical conversion of Hg clusters.

In the current Communication, we present the results of our investigations of the reaction of $Hg(TePh)_2$ with M′ (M′ = Ag^I, Co^{II}, Ni^{II}) salts stabilized by different phosphines (PPh_3 or PMe_2Ph) in dimethylformamide (DMF). We describe herein the synthesis and characterization of the clusters $[Hg_6Ag_4(TePh)_{16}]$ (**1**), $[Hg_6Ag_4Te(TePh)_{14}]_n$ (**2**), and $[Hg_8Te(TeC_6H_5)_{12}Cl_4]Q$ [**3**; Q = $[Co(DMF)_6]^{2+}$ (**3a**), $[Ni(dmf)_6]^{2+}$ (**3b**)].

The reaction of $Hg(TePh)_2$ and metal salts stabilized by phosphine ligands or solvent molecules should lead to different redistribution reactions with the simultaneous formation of PhTeHgX, $[(TePh)_2HgX]^-$, and $(TePh)[M(L)_n]$ (M = Ag, Co, Ni; L = $PMePh_2$, PPh_3, DMF) moieties.[7,9]

The reaction of $Hg(TePh)_2$ with $[Ag(L)_n]X$ (X = Cl^-, NO_3^-; L = $PMePh_2$, PPh_3, DMF) in a ratio of 1:2 at room temperature affords the cluster **1**, shown in Figure 1, with incorporation of Ag^I into the cluster structure.

Because of the labile nature of the ligands bonded to the Ag center in $[Ag(L)_n]^+$ and in conjunction with the expected reactivity of $Hg(TePh)_2$,[4,6] we assume that both reagents would be sources of $[PhTeAg(L)_n]$ moieties, providing the second metal to promote Hg−Te−Ag interactions in the synthesis of a ternary cluster. When the same reaction is carried out in the presence of $[Ag(PMePh_2)_2]X$ (X = Cl^-, NO_3^-) at 75−80 °C, the product obtained is the cluster **2** (Figure 2).

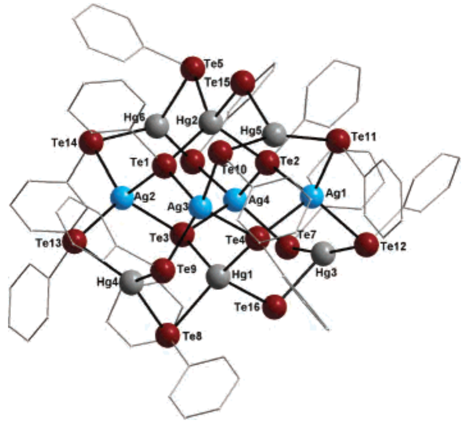

Figure 2. Structure of **2** (the H atoms are omitted, and the C atoms are represented as sticks for clarity).

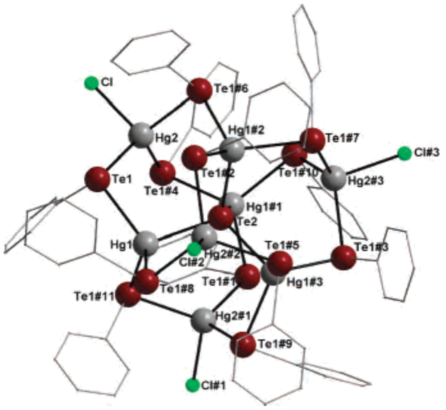

Figure 3. Structure of **3** (the H atoms are omitted, and the C atoms are represented as sticks for clarity).

The reaction of $Hg(TePh)_2$ with the complex $[Co(L)_nCl_2]$ or $[Ni(L)_nCl_2]$ (L = PMe_2Ph, PPh_3, DMF; n = 2, 4, 6) generates the anionic cluster $[Hg_8Te(TeC_6H_5)_{12}Cl_4]^{2-}$ stabilized by the cation $[Co(DMF)_6]^{2+}$ (**3a**) or $[Ni(DMF)_6]^{2+}$ (**3b**), respectively. The compounds **3a** and **3b** show that the Co^{II} and Ni^{II} complexes supply only Cl atoms to generate the anionic cluster $[Hg_8Te(TeC_6H_5)_{12}Cl_4]^{2-}$. This suggests that this reaction does not involve the incorporation of a second metal into the cluster. The effect of the variation of the M salts on the stability and reactivity of the precursor of the cluster seems to define the formation of a binary or ternary cluster. At the end of the reactions, only the product clusters, starting materials, and side products HgTe and $TePh_2$ are present.

The X-ray crystal structure of the cluster **1** (Figure 1) shows a central arrangement of metal and chalcogen ions, generating a tetrahedral framework consisting of fused $\{M_2M'_2\,E_6\}$ adamantine-type units, similar to the building blocks that constitute the architecture of the clusters $[M_{10}E_4(EPh)_{12}(P^nPr_3)_4]$ (M = Zn, Cd; M′ = Cd, Hg; E = Se, Te).[3a] The Ag atoms are located in the equatorial position

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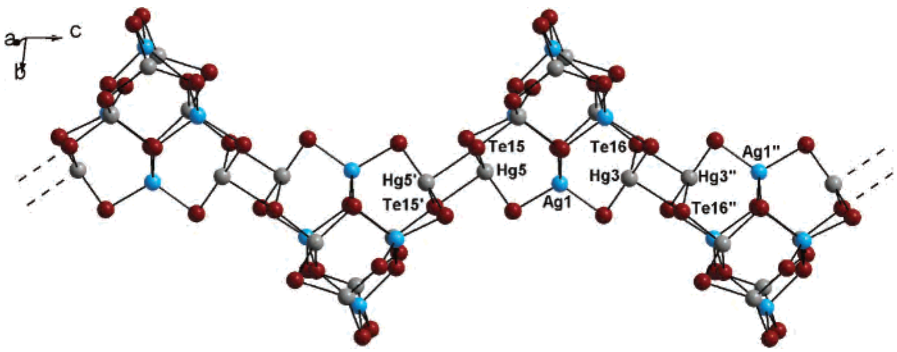

Figure 4. Structure of **2** with a disordered μ_2-Te atom appearing in two positions (Te15 and Te16) with an occupancy of 0.5 for each Te atom showing a pseudopolymeric structure in the direction of the crystallographic axis *c* (phenyl rings are omitted for clarity).

in the middle of the cluster linking two $\{Hg_3(TePh)_8\}$ moieties through Te−Ag bonds.

At first glance, the cluster **2** (Figure 2) is quite similar to **1**, however with two TePh units replaced by one μ_2-Te atom. The situation is a little more complicated because the μ_2-Te atom is disordered over the two positions within the cluster (Te15 and Te16), each with an occupancy of 0.5, with the possibility of forming bridges to nearby Hg atoms (Hg5 and Hg3, respectively) between two molecules of the cluster. If the disordered Te atoms are considered to alternate between the two possible positions to form single bridges between neighboring clusters, the resulting structure would be a one-dimensional zigzag chain of $[Hg_6Ag_4Te(TePh)_{14}]$ units along the direction of the crystallographic axis *c* (Figure 4). However, the bridging Te atoms also may be thought to occupy positions on adjacent clusters; thus, double bridges would be formed to result in a chain of the dimeric structure $[Hg_6Ag_4(TePh)_{14}(\mu\text{-Te})_2Hg_6Ag_4(TePh)_{14}]$; the positions of the double bridges would necessarily alternate between chains. The polymeric motif $[Hg_6Ag_4Te(TePh)_{14}]$ and the dimerized motif $[Hg_6Ag_4(TePh)_{14}(\mu\text{-Te})_2Hg_6Ag_4(TePh)_{14}]$ would be produced simultaneously in the structure. In this manner, depending on the occupancy of the bridging Te atom, a charge density wave character in the chains with an alternating double Te−Hg bridge between the clusters results.

In the isotypic $[Hg_8Te(TePh)_{12}Cl_4]^{2-}$ clusters (**3**) stabilized by the $[Co(DMF)_6]^{2+}$ (**3a**, Figure 3) or $[Ni(DMF)_6]^{2+}$ (**3b**) ion, the arrangement of the metal atoms and the phenyltellurium moieties in the $\{Hg_8Te(TePh)_{12}\}$ moieties consists of an architecture quite similar to those of $[Hg_8(^nPrTe)_{12}(\mu\text{-Br})Br_3]$,[9] where the eight Hg atoms present a distorted cubic arrangement with the dicoordinated μ-Br atom in the center. In the case of **3**, the eight Hg atoms exhibit a distorted square antiprismatic arrangement, with a four-coordinated μ_4-Te atom in the center, creating a perfect tetrahedral coordination geometry.

In this report, we have demonstrated the use of $Hg(TePh)_2$ as a precursor for the preparation of ternary clusters. This could be a complementary methodology for silyl reagents. Because this approach should be extensible to the synthons of the general formula $M(ER)_n$ for which the examples M = Mg, Bi, Ga, In, Sn, Sb, Zn, Cd, Hg, Au, Yb, Zr, Hf; E = S, Se, Te; and R = aryl, alkyl have been reported,[5,11] we predict that a systematic methodology for the synthesis of ternary clusters would be possible.

Acknowledgment. This work was supported with funds from PRONEX-CNPq/FAPERGS (Brazil).

Supporting Information Available: Detailed experimental section including the synthetic procedure and information of the equipment used, crystallographic information, and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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