

Communications

Synthesis and Structural Characterization of $[\text{PPh}_4]_2[\text{NET}_4][\text{AgTe}_7]$ and $[\text{PPh}_4]_2[\text{HgTe}_7]$, Compounds Containing the Unprecedented $\eta^3\text{-Te}_7^{4-}$ Anion

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While the chemistry of sulfidometalates and selenometalates has afforded many amazing species, for example $[\text{Re}_4\text{S}_4(\text{S}_3)_6]^{4-}$ and $[\text{V}_2\text{Se}_{13}]^{2-}$,² the bonding in these species is conventional, consisting of liganded Q_n^{2-} moieties ($\text{Q} = \text{S}, \text{Se}; n \geq 1$). Despite the paucity of known species, it is the chemistry of the tellurometalates that appears to harbor the most unconventional bonding arrangements. Thus, $[\text{AuTe}_7]^{3-}$ can be thought of as possessing an $\eta^3\text{-Te}_5^{4-}$ ligand as well as an $\eta^1\text{-Te}_2^{2-}$ ligand,³ neither of which has sulfur or selenium counterparts, while the bonding arrangement in the $[\text{NbTe}_{10}]^{3-}$ anion defies description.⁴ We now describe two new anions, $[\text{AgTe}_7]^{3-}$ and $[\text{HgTe}_7]^{2-}$, each of which consists of a metal center coordinated by a single $\eta^3\text{-Te}_7^{4-}$ ligand, a previously unknown ligand with no sulfur or selenium analogues.

Polytelluride solutions were prepared by dissolving Li_2Te powder (prepared from the stoichiometric amounts of the elements in liquid ammonia) and 3 equiv of Te powder in DMF. $[\text{PPh}_4]_2[\text{HgTe}_7]$ was prepared in the following manner. A polytelluride solution was added to a DMF solution of $\text{Hg}(\text{xan})_2$ ($\text{xan} = \text{S}_2\text{COEt}$) and PPh_4Cl with stirring. Triethylphosphine was added, and the mixture was heated for 1 h at 90 °C, followed by filtration and layering with ether. $[\text{PPh}_4]_2[\text{NET}_4][\text{AgTe}_7]$ was

obtained when another polytelluride solution, similar except for the addition of a small amount of metallic sodium, was added to a DMF solution of $[\text{AgI}(\text{PMe}_3)]_4$ and triethylphosphine, followed by addition of NET_4Cl and PPh_4Cl . If neither sodium nor PPh_4Cl is used, then only $[\text{NET}_4]_4[(\text{Te}_4)\text{Ag}(\mu\text{-Te}_4)\text{Ag}(\text{Te}_4)]$ is isolated.⁵

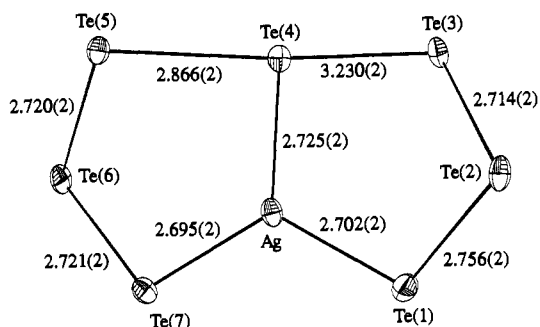


Figure 1. View of the $[\text{AgTe}_7]^{3-}$ ion with the 50% probability thermal ellipsoids shown. Important bond angles: $\text{Te}(3)\text{-Te}(4)\text{-Te}(5)$, $174.12(5)^\circ$; $\text{Ag}\text{-Te}(4)\text{-Te}(3)$, $89.41(5)^\circ$; $\text{Ag}\text{-Te}(4)\text{-Te}(5)$, $95.52(5)^\circ$; $\text{Te}(1)\text{-Ag}\text{-Te}(4)$, $124.48(6)^\circ$; $\text{Te}(1)\text{-Ag}\text{-Te}(7)$, $119.45(6)^\circ$; $\text{Te}(4)\text{-Ag}\text{-Te}(7)$, $116.07(6)^\circ$.

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- Crystal data for $[\text{PPh}_4]_2[\text{NET}_4][\text{AgTe}_7]$: $\text{C}_{56}\text{H}_{60}\text{AgNP}_2\text{Te}_7$, triclinic $C_1^1\text{-P1}$, $Z = 2$, $a = 8.893(2)$ Å, $b = 14.663(4)$ Å, $c = 23.320(6)$ Å, $\alpha = 87.17(1)^\circ$, $\beta = 80.74(1)^\circ$, $\gamma = 75.82(1)^\circ$, $V = 2910(1)$ Å³ at -165 °C. $R_w(F^2) = 0.148$ for 320 variables and 8626 independent reflections; $R(F) = 0.071$ for 5470 reflections having $F_o^2 > 2\sigma(F_o^2)$. Crystal data for $[\text{PPh}_4]_2[\text{HgTe}_7]$: $\text{C}_{48}\text{H}_{40}\text{HgP}_2\text{Te}_7$, monoclinic $C_{2h}^2\text{-P2}_1/n$, $Z = 2$, $a = 12.755(3)$ Å, $b = 14.327(3)$ Å, $c = 13.932(3)$ Å, $\beta = 105.58(3)^\circ$, $V = 2452(1)$ Å³ at -163 °C. $R_w(F^2) = 0.097$ for 289 variables and 4292 independent reflections; $R(F) = 0.046$ for 3708 reflections having $F_o^2 > 2\sigma(F_o^2)$. The structures were refined against F_o^2 by full-matrix least-squares methods (Sheldrick, G. M. SHELXL-92 Unix Beta-test Version, 1992). The $[\text{HgTe}_7]^{2-}$ ion is disordered over a center of inversion, with each atom having an occupancy of 0.50 except for Te(2), which has an occupancy of 1.0 because it cannot be resolved from what is Te(6) in the Ag complex. The assignment of atom positions to the $[\text{HgTe}_7]^{2-}$ anion or its inverted image was made with reference to the geometry derived from the $[\text{AgTe}_7]^{3-}$ anion.

The phosphine provides the requisite basic medium and may solubilize any metallic tellurium formed during the course of the reaction.

The $[\text{AgTe}_7]^{3-}$ and $[\text{HgTe}_7]^{2-}$ ions are shown in Figures 1 and 2, respectively.⁶ The metals have trigonal planar coordination. With the exception of atoms Te(2) and Te(6) in $[\text{AgTe}_7]^{3-}$ and atoms Te(2) and Te(2a) in $[\text{HgTe}_7]^{2-}$, the anions are planar, the average deviation of the MTe_5 moiety from planarity being 0.108 Å for $\text{M} = \text{Ag}$ and 0.111 Å for $\text{M} = \text{Hg}$. There are many examples of trigonal planar coordination of chalcogens about Ag(I) and Hg(II),^{5,7-10} while such a bonding arrangement is unknown for Hg(I). To assign a higher oxidation state to Ag requires a ligand with charge greater than 4. Thus, we assign metal oxidation states of Ag(I) and Hg(II), leading to the formulation of the ligand as $\eta^3\text{-Te}_7^{4-}$, and we believe it is possible to rationalize the nature of the bonding in the $\eta^3\text{-Te}_7^{4-}$ ligand.

The most intriguing feature of the anions is the T-shaped bonding pattern around atom Te(4). The $\text{Te}(3)\text{-Te}(4)\text{-Te}(5)$ angles are $174.12(5)$ and $174.52(5)^\circ$ in the Ag and Hg anions, respectively. The $\text{M}\text{-Te}(4)\text{-Te}(3,5)$ angles are $89.41(5)$ and

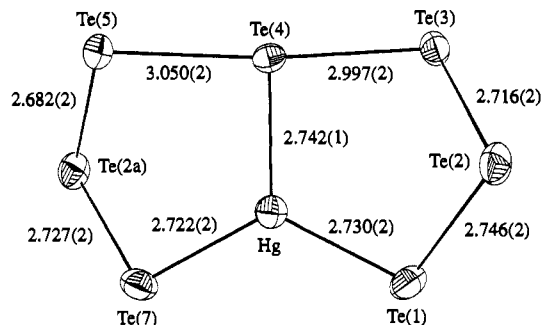


Figure 2. View of the $[\text{HgTe}_7]^{2-}$ ion with the 50% probability thermal ellipsoids shown. Important bond angles: $\text{Te}(3)\text{--Te}(4)\text{--Te}(5)$, $174.52(5)^\circ$; $\text{Hg--Te}(4)\text{--Te}(3)$, $92.75(4)^\circ$; $\text{Hg--Te}(4)\text{--Te}(5)$, $92.68(5)^\circ$; $\text{Te}(1)\text{--Hg--Te}(4)$, $117.70(5)^\circ$; $\text{Te}(1)\text{--Hg--Te}(7)$, $124.37(5)^\circ$; $\text{Te}(4)\text{--Hg--Te}(7)$, $117.92(4)^\circ$.

$95.52(5)^\circ$ in the Ag complex and $92.75(4)$ and $92.68(5)^\circ$ in the Hg compound. The $\text{M--Te}(4)$ distances in the two compounds are similar to the other M--Te distances in each complex; Ag--Te distances range from $2.695(2)$ to $2.725(2)$ Å, and the Hg--Te distances range from $2.722(2)$ to $2.742(1)$ Å. However, the $\text{Te}(4)\text{--Te}$ distances differ dramatically from the other Te--Te distances in the two complexes. In the Ag complex the $\text{Te}(4)\text{--Te}(3)$ and the $\text{Te}(4)\text{--Te}(5)$ distances are $3.230(2)$ and $2.866(2)$ Å, respectively, while the remaining Te--Te distances vary from $2.714(2)$ to $2.756(2)$ Å. In the Hg compound the $\text{Te}(4)\text{--Te}(3)$ and the $\text{Te}(4)\text{--Te}(5)$ distances are $2.997(2)$ and $3.050(2)$ Å, respectively, while the remaining Te--Te distances vary from $2.682(2)$ to $2.746(2)$ Å. The longer bond lengths around $\text{Te}(4)$ are expected if $\text{Te}(3)$, $\text{Te}(4)$, and $\text{Te}(5)$ are joined by a three-center four-electron bond, while the $\text{Te}(3)\text{--Te}(2)$ and $\text{Te}(5)\text{--Te}(6)$ bonds are normal two-center two-electron bonds. The bonding about atom $\text{Te}(4)$ is unsymmetrical in the Ag compound, but it is symmetrical in the Hg compound. Although we offer no explanation for this, we note that the closely related I_3^- anion shows at times symmetrical bonding and at other times unsymmetrical bonding.¹¹ The $\text{Te}(4)\text{--Te}(3)$ distance of $3.230(2)$ Å in the Ag complex is long, but to describe it as a nonbond is to ignore similar distances seen in polyiodide anions.¹¹ Moreover, if it is

not a bond this implies the very unlikely $\eta^1\text{-Te}_3$ ligand, and one must somehow explain the presence of atom $\text{Te}(3)$ in the AgTe_5 plane.

The $\eta^3\text{-Te}_7^{4-}$ chelate is a new polychalcogenide ligand. The compounds $\text{M}(\text{S}_7)(\text{PMe}_3)_3$ ($\text{M} = \text{Ru}, \text{Os}$)¹² contain the $\eta^3\text{-S}_7^{2-}$ ligand. These complexes are diamagnetic, as expected for metal centers with a d^6 configuration (S_7^{2-}) but not for those with a d^4 configuration (S_7^{4-}). Nor does the three-coordinate S atom in the $\eta^3\text{-S}_7^{2-}$ chelate exhibit T-shaped bonding, but rather it has the normal bond lengths and angles found around most three-coordinate S atoms. Why this difference on going from S to Te? Comparisons with the halogens suggest the increased atomic size and polarizability and decreased p-to-d promotional energy in Te influence this behavior.¹¹ The VSEPR model would describe orbitals around the $\text{Te}(4)$ atom as sp^3d hybridized. The VSEPR model is known to overestimate d-orbital contributions to bonding, and the molecular orbital approach of a three-center four-electron bond around atom $\text{Te}(4)$ is preferable. Application of delocalized orbitals to the isoelectronic species I_3^- ¹¹ and XeF_2 ¹³ indicates the bond consists primarily of p orbitals, with only minor contributions from the s and d orbitals. The bonding description with atom $\text{Te}(4)$ being part of a three-center four-electron system implies that atom $\text{Te}(4)$ is hypervalent with 10 electrons and that it donates electrons to a metal center. To our knowledge such bonding is unprecedented but then so is an $\eta^3\text{-Te}_7^{4-}$ species. The few examples of tellurometalates suggest that a rich reaction and structural chemistry remains to be uncovered.

Note Added in Proof: Müller, et al.¹⁴ have just reported the preparation and structures of the $[\text{K}(15\text{-crown-5})]^+$ salts of $[\text{ZnTe}_7]^{2-}$ and $[\text{HgTe}_7]^{2-}$. While these compounds exhibit two-dimensional disorder, the average structure of the $[\text{HgTe}_7]^{2-}$ anion closely resembles the structures reported here and is described by them as consisting of two condensed five-membered rings. The average structure of the $[\text{ZnTe}_7]^{2-}$ anion is different and is described by them as consisting of Zn^{2+} ion coordinated in a bidentate manner to a Te_4^{2+} ion and in a monodentate manner to a Te_3^{2-} ion.

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Supplementary Material Available: Crystallographic details (Table SI), positional parameters (Tables SII and SIII), thermal displacements (Tables SIV and SV), and bond distances and angles (Table SVI and SVII) (15 pages). Ordering information is given on any current masthead page.

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