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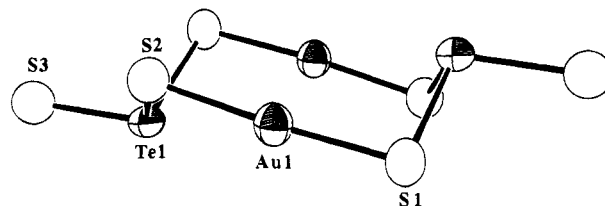
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The polysulfide, polyselenide, and polytelluride anions  $\text{Q}_n^{2-}$  ( $\text{Q} = \text{S}, \text{Se}, \text{and Te}; n = 2\text{--}6$ ) rank among the most versatile chelating ligands for transition metal ions.<sup>1,2</sup> These so-called Zintl ions are readily produced through reactions of electropositive metals with elemental chalcogens.<sup>3</sup> The homoatomic bonding in such anions represents a retention, to a certain degree, of the characteristics of the element. On the other hand, the structure and bonding of the heterochalcogenide anions, complicated by redox chemistry, is expected to be rather different. The large size difference between S and Te and the preference of each to stabilize a different lattice should result in mixed S/Te-containing compounds in which these elements would occupy well-defined ordered sites and not be positionally disordered. Recently, we proposed that compounds containing various proportions of S and Te may adopt new structures representing a compromise between the two different structure-directing tendencies of S and Te.<sup>4</sup> We have shown that in a S-rich environment Te acts as a metalloid being oxidized and then coordinated by sulfide ions.<sup>5</sup> Thus, instead of forming a mixed S/Te polychalcogenide chain, a pyramidal isomeric structure occurs,  $[\text{TeS}_3]^{2-}$ , which places the Te at the apex surrounded by three sulfide ions. The redox behavior is a consequence of the electronegativity difference between S and Te. Despite the recent extensive development in the homopolychalcogenide chemistry, much less is known about the chemistry of the heterochalcogenide systems involving species such as  $[\text{Te}_x\text{S}_y]^{2-}$  and  $[\text{Te}_x\text{Se}_y]^{2-}$ .<sup>6</sup> This prompted us to investigate the metal heterochalcogenide chemistry in the solid state as well as in polar organic solvents.<sup>4,5</sup> We began our studies of solution chemistry with the reactions of two coinage metal ions  $\text{Ag}^+$  and  $\text{Au}^+$  with two simple alkali tellurium sulfide/selenide compounds  $\text{K}_2\text{TeS}_3$  and  $\text{K}_2\text{TeSe}_3$ . In this communication, we wish to report the synthesis and X-ray structures of  $(\text{Me}_4\text{N})_2[\text{Au}_2(\text{TeS}_3)_2]$  (**1**),  $(\text{Ph}_3\text{P})_2\text{N}_2[\text{Ag}_2\text{Te}(\text{TeS}_3)_2]\cdot\text{DMF}$  (**2**), and  $(\text{Ph}_4\text{P})_2[\text{Ag}_2\text{Te}(\text{TeSe}_3)_2]$  (**3**).

Compound **1** was prepared by reacting AuCN with  $(\text{Me}_4\text{N})_2\text{TeS}_3$  in DMF at 23 °C.<sup>7</sup> The crystal lattice of **1** is made up of noninteracting  $\text{Me}_4\text{N}^+$  cations and  $[\text{Au}_2(\text{TeS}_3)_2]^{2-}$  anions.<sup>8</sup> The  $[\text{Au}_2(\text{TeS}_3)_2]^{2-}$  anion, shown in Figure 1, has a ring structure



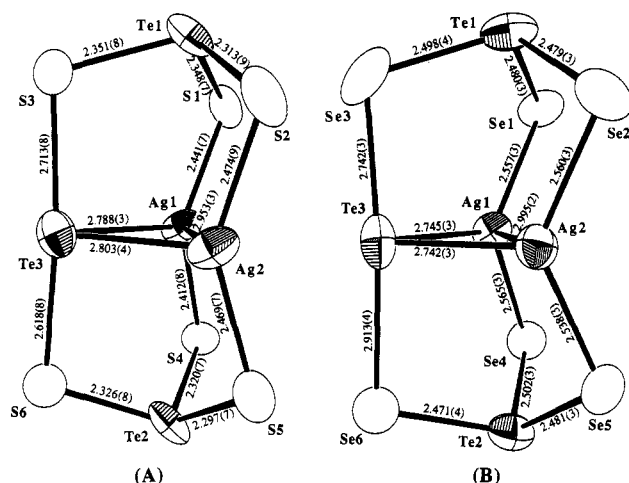
**Figure 1.** Structure of  $[\text{Au}_2(\text{TeS}_3)_2]^{2-}$ . Selected bond distances (Å) and angles (deg): Au1–S1, 2.280(7); Au1–S2, 2.302(7); Te1–S1, 2.378(8); Te1–S2, 2.372(8); Te1–S3, 2.272(8); S1–Au1–S2, 174.8(3); S1–Te1–S2, 100.6(3); S1–Te1–S3, 102.2(3); S2–Te1–S3, 102.7(3); Au1–S1–Te1, 99.2(2); Au1–S2–Te1, 95.3(3).

and features two linearly coordinated  $\text{Au}^+$  centers bridged by two  $\text{TeS}_3^{2-}$  ligands. The latter has a pyramidal shape and acts as bidentate ligand, forming an eight-membered ring with the  $\text{Au}^+$  centers. Due to the linear coordination of  $\text{Au}^+$ , the conformation of this ring can be best described as chair form similar to the most stable conformation of cyclohexane. Furthermore, if the molecule is viewed as a 1,6-disubstituted cyclohexane analog, both noncoordinated S atoms occupy the equatorial positions. The molecule has a  $\text{C}_{2h}$  symmetry with a noncrystallographic 2-fold axis running across  $\text{Au}\cdots\text{Au}^*$  and the mirror running through  $\text{S3/Te/Te}^*/\text{S3}^*$ . The bond distance of the Te atom to the noncoordinated S is shorter than those found in the ring, suggesting some double bond character. The solid-state far-IR spectrum (CsI matrix) shows characteristic Te–S stretching vibrations at 334, 343, and 403  $\text{cm}^{-1}$ . The Au–S stretching vibration usually arising around 325  $\text{cm}^{-1}$  is masked by the strong Te–S stretching bands.

The synthesis of  $[(\text{Ph}_3\text{P})_2\text{N}]_2[\text{Ag}_2\text{Te}(\text{TeS}_3)_2]\cdot\text{DMF}$  (**2**) was accomplished by reacting  $\text{AgNO}_3$  with  $\text{K}_2\text{Te}$  and elemental S in the presence of  $[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$  in DMF at 23 °C.<sup>9</sup>  $(\text{Ph}_4\text{P})_2[\text{Ag}_2\text{Te}(\text{TeSe}_3)_2]$  (**3**) was prepared using  $\text{AgBF}_4$ ,  $\text{K}_2\text{Se}_3$ , elemental Te, and  $\text{Ph}_4\text{PBr}$ .<sup>10</sup> The isostructural anions<sup>11</sup> in **2** and **3** adopt a novel cage structure assembled by a triangular  $\text{Ag}_2\text{Te}$  plane sandwiched by two pyramidal  $\text{TeQ}_3^{2-}$  ( $\text{Q} = \text{S}, \text{Se}$ ) units, as shown in Figure 2. The coordination geometry of the Ag atoms strongly deviates from the linear motif adopted by the Au atoms in **1**. The S–Ag–S angles average 143.6°, while the Se–Ag–

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- (7)  $(\text{Me}_4\text{N})_2[\text{Au}_2(\text{TeS}_3)_2]$  (**1**):  $\text{K}_2\text{TeS}_3$  was prepared using stoichiometric amount of elemental K, Te, and S in liquid ammonia.  $\text{K}_2\text{TeS}_3$  and 2 equiv of  $\text{Me}_4\text{NCl}$  were dissolved in water and filtered, resulting in a yellow solution. The filtrate was evaporated to dryness to give a yellowish green powder. The powder of  $(\text{Me}_4\text{N})_2\text{TeS}_3$  was recrystallized from methanol–ether and dried. To a solution of  $(\text{Me}_4\text{N})_2\text{TeS}_3$  (100 mg, 0.27 mmol) in 20 mL of DMF was added dropwise a 15-mL DMF solution containing AuCN (60 mg, 0.27 mmol). The mixture was stirred for 1 day and filtered to remove a black powder. The green filtrate was layered with 50 mL of ether to induce crystallization of yellow leaf-shaped crystals of  $(\text{Me}_4\text{N})_2[\text{Au}_2(\text{TeS}_3)_2]$ . Quick precipitation gives the product in 45% yield based on the AuCN.
- (8) Single-crystal X-ray diffraction data for  $(\text{Me}_4\text{N})_2[\text{Au}_2(\text{TeS}_3)_2]$  were collected at 23 °C on a Rigaku AFC6 diffractometer. Data are as follows: monoclinic  $P2_1/c$  (No. 14);  $a = 6.582(3)$  Å,  $b = 18.936(5)$  Å,  $c = 9.148(1)$  Å,  $\beta = 101.52(2)^\circ$ ,  $Z = 2$ ,  $V = 1117.4(6)$  Å<sup>3</sup>,  $d_{\text{calc}} = 2.940$  g/cm<sup>3</sup>;  $\mu = 161.66$  cm<sup>−1</sup>,  $2\theta_{\text{max}}(\text{Mo K}\alpha) = 45.0^\circ$ ; total data collected 1671, unique data 1522, data with  $F_o^2 > 3\sigma(F_o^2)$  932; final  $R = 4.5\%$ ,  $R_w = 5.6\%$ . The structure was solved using software described elsewhere.<sup>5</sup>



**Figure 2.** (A) Structure of  $[\text{Ag}_2\text{Te}(\text{TeS}_3)_2]^{2-}$ . Selected bond angles (deg): S1–Te1–S2, 104.5(3); S1–Te1–S3, 103.6(2); S2–Te1–S3, 105.8(3); S4–Te2–S5, 104.5(3); S4–Te2–S6, 104.4(3); S5–Te2–S6, 103.8(3); Ag2–Ag1–Te3, 58.36(8); Te3–Ag1–S4, 108.5(2); S1–Ag1–S4, 141.0(3); Ag1–Ag2–Te3, 57.88(8); Te3–Ag2–S2, 106.9(2); Te3–Ag2–S5, 106.4(2); S2–Ag2–S5, 146.2(3); Ag1–Te3–Ag2, 63.76(8); S3–Te3–S6, 173.6(3); Te1–S1–Ag1, 101.3(2); Te1–S2–Ag2, 101.7(3); Te1–S3–Te3, 104.4(3); Te2–S4–Ag1, 99.8(3); Te2–S5–Ag2, 104.0(3); Te2–S6–Te3, 106.0(3). (B) Structure of  $[\text{Ag}_2\text{Te}(\text{TeSe}_3)_2]^{2-}$ . Selected bond angles (deg): Se1–Te1–Se2, 102.1(1); Se1–Te1–Se3, 104.3(1); Se2–Te1–Se3, 105.3(1); Se4–Te2–Se5, 105.4(1); Se4–Te2–Se6, 103.6(1); Se5–Te2–Se6, 104.7(1); Ag2–Ag1–Te3, 56.87(6); Se1–Ag1–Se4, 129.3(1); Ag1–Ag2–Te3, 56.96(6); Ag1–Ag2–Se2, 102.72(9); Ag1–Ag2–Se5, 94.57(8); Te3–Ag2–Se2, 114.0(1); Te3–Ag2–Se5, 112.74(9); Se2–Ag2–Se5, 132.3(1); Ag1–Te3–Ag2, 66.17(7); Se3–Te3–Se6, 173.9(1); Te1–Se1–Ag1, 99.2(1); Te1–Se2–Ag2, 96.8(1); Te1–Se3–Te3, 104.3(1); Te2–Se4–Ag1, 94.3(1); Te2–Se5–Ag2, 102.01(9); Te2–Se6–Te3, 102.6(1).

Se angles are even narrower at  $130.8^\circ$ . The unusual structural feature of these two complexes is the presence of the linear Q3–Te3–Q3 fragment which is disposed perpendicular to the  $\text{Ag}_2\text{Te}$  plane. The bent geometries around the Ag atoms are due to the size mismatch of the  $\text{Ag}_2\text{Te}$  triangle and the all-S or all-Se triangle forming the base of the  $\text{TeQ}_3^{2-}$  pyramid. If we

assign formal charges of +1 to the two Ag atoms and –2 to the two pyramidal  $\text{TeQ}_3$  units, then the formal charge on Te3 must be zero. This is consistent not only with its long Te3–S and Te3–Se bonds but also with the linear coordination of this atom. The linear Q3–Te3–Q3 fragment is isoelectronic to  $\text{I}_3^-$  (we view it to consist of two  $\text{I}^-$  ions bonding to a  $\text{I}^+$  center). In this context, it must be noted that the heterochalcogenide bonding in  $[\text{Ag}_2\text{Te}(\text{TeQ}_3)_2]^{2-}$  seems similar in nature to the homochalcogenide bonding found in  $[\text{AgTe}_7]^{3-}$ ,<sup>12</sup> and  $[\text{MTe}_7]^{3-}$  ( $\text{M} = \text{Hg},^{12,13} \text{Zn}^{13}$ ). The Ag–Ag distances at 2.953 and 2.995 Å are not unusually short to amount to anything more than the familiar  $d^{10}$ – $d^{10}$  interaction. The Ag–Te3 distances, however, vary narrowly around 2.77 Å in both compounds, and this is well within the range of normal Ag–Te bonds.<sup>14</sup> All bond distances and angles in  $\text{TeQ}_3^{2-}$  are within the range of normal values which were known in the  $\text{TeQ}_3^{2-}$  salts.<sup>4,5,15</sup>

To further characterize the new ligand  $\text{Te}(\text{TeQ}_3)_2^{4-}$ , we performed  $^{125}\text{Te}$  NMR spectroscopy<sup>16</sup> on  $(\text{Ph}_4\text{P})_2[\text{Ag}_2\text{Te}(\text{TeSe}_3)_2]$ . Two different types of Te atoms are observed as expected at 874.7 and –488.4 ppm. The Te–S and Te–Se stretching vibrations are observed at 356 and 237  $\text{cm}^{-1}$ , respectively.

Exploratory reactions in the system  $\text{Ph}_4\text{P}^+/\text{Cu}^+/\text{TeQ}_3^{2-}$  gave a new complex which possibly contains the same anion as 2 and 3 but possesses a different X-ray powder diffraction pattern.<sup>17</sup>

In conclusion, the heteropolychalcogenides,  $\text{TeQ}_3^{2-}$ , are novel structural units which bear little resemblance to their homopolychalcogenide brethren. They belong to a separate class more closely akin to that of the tetrathiometalates. The ability of heteropolychalcogenides to form linked fragments such as the  $[\text{Q}_2\text{TeQ}–\text{Te}–\text{QTeQ}_2]^{4-}$  may extend to longer analogs and forecasts an unexpected but welcome new direction for the coordination chemistry of polychalcogenides.

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**Supporting Information Available:** Tables of crystallographic details, positional parameters, bond distances and angles, anisotropic and isotropic thermal parameters of all non-hydrogen atoms, and calculated and observed X-ray powder diffraction patterns for all compounds (36 pages). Ordering information is given on any current masthead page.

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- (9)  $[(\text{Ph}_3\text{P})_2\text{N}]_2[\text{Ag}_2\text{Te}(\text{TeS}_3)_2]\cdot\text{DMF}$  (2): An amount of 20 mL of a DMF solution of  $\text{K}_2\text{Te}$  (100 mg, 0.49 mmol), elemental S (47 mg, 1.47 mmol), and  $[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$  (200 mg, 0.35 mmol) was stirred overnight until complete reaction had taken place. To this solution was added dropwise a 10-mL DMF solution of  $\text{AgNO}_3$  (80 mg, 0.47 mmol), and the solution mixture was stirred overnight. A dark brown precipitate was removed by filtration, and the blue filtrate was layered with 100 mL of ether to give red needle crystals of  $[(\text{Ph}_3\text{P})_2\text{N}]_2[\text{Ag}_2\text{Te}(\text{TeS}_3)_2]\cdot\text{DMF}$  in 5 days. Quick precipitation yields approximately 56% based on the  $\text{AgNO}_3$ . Anal. Calcd for  $\text{C}_{76}\text{H}_{67}\text{P}_4\text{N}_2\text{OAg}_2\text{Te}_3\text{S}_6$ : C, 46.35; H, 3.45; P, 6.38; Ag, 11.1; Te, 19.72; S, 9.90. Found: C, 45.99; H, 3.52; P, 7.35; Ag, 9.66; Te, 19.56; S, 9.77.
- (10) The preparation of  $(\text{Ph}_4\text{P})_2[\text{Ag}_2\text{Te}(\text{TeSe}_3)_2]$  (3) was carried out using  $\text{K}_2\text{Se}_3$  (150 mg, 0.48 mmol), elemental Te (91 mg, 0.71 mmol),  $\text{AgBF}_4$  (93 mg, 0.48 mmol), and  $\text{Ph}_4\text{PBr}$  (210 mg, 0.50 mmol) under the same conditions as described for  $[(\text{Ph}_3\text{P})_2\text{N}]_2[\text{Ag}_2\text{Te}(\text{TeS}_3)_2]\cdot\text{DMF}$ . The total yield was 62% based on  $\text{AgBF}_4$ . Anal. Calcd for  $\text{C}_{48}\text{H}_{40}\text{P}_2\text{Ag}_2\text{Te}_3\text{Se}_6$ : Ag, 12.32; Te, 21.86; Se, 27.05. Found: Ag, 11.82; Te, 20.42; Se, 27.75.
- (11) (a) Data for  $[(\text{Ph}_3\text{P})_2\text{N}]_2[\text{Ag}_2\text{Te}(\text{TeS}_3)_2]\cdot\text{DMF}$  were collected at  $-90^\circ\text{C}$  on a computer-controlled four-circle Nicolet (Siemens) autodiffractometer. Data are as follows: monoclinic  $P2_1/c$  (No. 14);  $a = 33.01(2)$  Å,  $b = 12.569(4)$  Å,  $c = 21.618(4)$  Å,  $\beta = 123.20(3)^\circ$ ,  $Z = 4$ ,  $V = 7506(5)$  Å<sup>3</sup>,  $d_{\text{calc}} = 1.717$  g/cm<sup>3</sup>;  $\mu = 19.52$  cm<sup>–1</sup>,  $2\theta_{\text{max}}(\text{Mo K}\alpha) = 49.8^\circ$ ; total data collected 19 556, unique data 10 341, data with  $F_o^2 > 3\sigma(F_o^2)$  3836; final  $R = 7.5\%$ ,  $R_w = 7.7\%$ . (b) Single-crystal X-ray diffraction data for  $(\text{Ph}_4\text{P})_2[\text{Ag}_2\text{Te}(\text{TeSe}_3)_2]$  were collected at  $23^\circ\text{C}$  on a Rigaku AFC6 diffractometer. Data are as follows: triclinic  $P\bar{1}$  (No. 2);  $a = 11.230(3)$  Å,  $b = 22.259(8)$  Å,  $c = 10.872(5)$  Å,  $\alpha = 93.01(3)^\circ$ ,  $\beta = 102.88(3)^\circ$ ,  $\gamma = 89.41(3)^\circ$ ,  $Z = 2$ ,  $V = 2646(2)$  Å<sup>3</sup>,  $d_{\text{calc}} = 2.198$  g/cm<sup>3</sup>;  $\mu = 65.39$  cm<sup>–1</sup>,  $2\theta_{\text{max}}(\text{Mo K}\alpha) = 45.0^\circ$ ; total data collected 7151, unique data 6914, data with  $F_o^2 > 3\sigma(F_o^2)$  3770; final  $R = 4.8\%$ ,  $R_w = 6.7\%$ .

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- (16)  $^{125}\text{Te}$  NMR spectroscopy was carried out in  $\text{DMSO}-d_6$  at  $25^\circ\text{C}$ , and chemical shifts are referenced to the  $^{125}\text{Te}$  signal of 1237 ppm for  $\text{TeCl}_4$  in  $\text{D}_2\text{O}/\text{HCl}$ .
- (17) (a) Unit cell of the amber platelet single crystals formed in the  $\text{Ph}_4\text{P}^+/\text{Cu}^+/\text{TeS}_3^{2-}$  system:  $a = 10.636(4)$  Å,  $b = 21.68(2)$  Å,  $c = 21.92(1)$  Å,  $\beta = 96.06(4)^\circ$ ,  $V = 5024(6)$  Å<sup>3</sup>. (b) Unit cell of the brown chunky single crystals formed in the  $\text{Ph}_4\text{P}^+/\text{Cu}^+/\text{TeSe}_3^{2-}$  system:  $a = 10.618(7)$  Å,  $b = 22.32(1)$  Å,  $c = 22.25(1)$  Å,  $\beta = 95.77(6)^\circ$ ,  $V = 5246(5)$  Å<sup>3</sup>.