

[TeSe₃]²⁻ and [TeSe₂]²⁻ as synthons

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The [Au₂(TeSe₂)₂]²⁻ anion has been prepared from the reaction of [TeSe₃]²⁻ with AuCN in DMF in the presence of PEt₃ and from the reaction of [TeSe₂]²⁻ with AuCN in DMF. Reaction of [TeSe₂]²⁻ with AuCN in DMF in the presence of PEt₃ leads ultimately to the [Au₂(Te₂)₂]²⁻ anion.

The known [Te_mSe_p]ⁿ⁻ anions include [TeSe₂]²⁻,¹ [TeSe₃]²⁻,^{1,2} [Te(Se₅)₂]²⁻,³ [Te(Se₅)₃]⁴⁻,⁴ [{Te(Se₂)₂]₂(μ₂-Se₂)]²⁻,^{4,5} and [Te₃Se₆]²⁻.⁵ All but the last anion contain Te^{II} or Te^{IV} centers bonded to Se_n²⁻ species (n = 1, 2, or 5). [Te₃Se₆]²⁻ consists of a one-dimensional infinite $\frac{1}{\infty}$ [Te(μ₂-Se₃)(μ₂-(SeTeSe)Te(μ₂-Se)²⁻)] chain separated by cations. Although the [Q_m]²⁻ (Q = S or Se or Te) polychalcogenide anions have been employed in the development of an extensive polychalcogenometalate solution chemistry,^{6–10} we can find only one report of a reaction with a metal system of a mixed Te/S or Te/Se polychalcogenide anion. Here we report the reactions of [TeSe₃]²⁻ and [TeSe₂]²⁻ with Au⁺ in DMF to afford the [Au₂(TeSe₂)₂]²⁻ anion as well as the [Au₂(Te₂)(Te_{2.39}Se_{0.61})]²⁻ and [Au₂(Te₂)₂]²⁻ anions.

[PPh₄]₂[Au₂(TeSe₂)₂] has been prepared by the reaction of AuCN with Na₂[TeSe₃] in DMF in the presence of excess PEt₃ and PPh₄Br at 20 °C.¹¹ The same compound can also be synthesized with KAUCN₂ in place of AuCN. However, when PEt₃ is omitted from either reaction no product is obtained. It is well known that PEt₃ is capable of extracting Se from polyselenides¹² and that is the case here as evidenced by a signal at δ = 47.2 ppm in the ³¹P NMR spectrum of the original reaction solution; this corresponds to a value of δ = 45 obtained earlier for SePEt₃.¹³ Presumably the other product is [TeSe₂]²⁻. The necessity of including PEt₃ in these reactions is to be contrasted with the direct reaction of [Me₄N]₂[TeS₃] with AuCN to afford the [Au₂(TeS₃)₂]²⁻ anion, in which the TeS₃ unit remains intact.¹⁴

The crystal structure of [PPh₄]₂[Au₂(TeSe₂)₂] comprises four [PPh₄]⁺ cations and two [Au₂(TeSe₂)₂]²⁻ anions well-separated in the unit cell.¹⁵ The structure of the [Au₂(TeSe₂)₂]²⁻ anion, which has crystallographically imposed $\bar{1}$ symmetry, together with selected bond distances and angles is shown in Fig. 1. The two TeSe₂ groups act as bidentate ligands to the two Au centers, resulting in essentially linear Se–Au–Se linkages and an eight-membered ring with a chair conformation. The Au...Au distance of 3.917 Å is too long for bonding.^{16,17} The [Au₂(TeSe₂)₂]²⁻ anion is conveniently described in a formal sense as [(Au⁺)₂(TeSe₂²⁻)₂]²⁻. The structure of [Au₂(TeSe₂)₂]²⁻ resembles that of [Au₂(TeS₃)₂]²⁻ reported earlier, although in that compound the Te center is bonded to three chalcogens.¹⁴

The likelihood that the polychalcogenide reactant that led to the formation of the [Au₂(TeSe₂)₂]²⁻ anion was not [TeSe₃]²⁻ but rather was [TeSe₂]²⁻ prompted us to carry out the reactions described above in the absence of PEt₃ but with Na₂[TeSe₂] in place of Na₂[TeSe₃]. As anticipated, the only product obtained was [PPh₄]₂[Au₂(TeSe₂)₂]. However, if PEt₃ was added to the reaction of Na₂[TeSe₂] with KAUCN₂ in DMF the compound [PPh₄]₂[Au₂(Te₂)(Te_{2.39}Se_{0.61})]¹⁸ (Fig. 2) was obtained. This compound is analogous to [PPh₄]₂[Au₂(Se₂)(Se₃)].¹⁹ In this

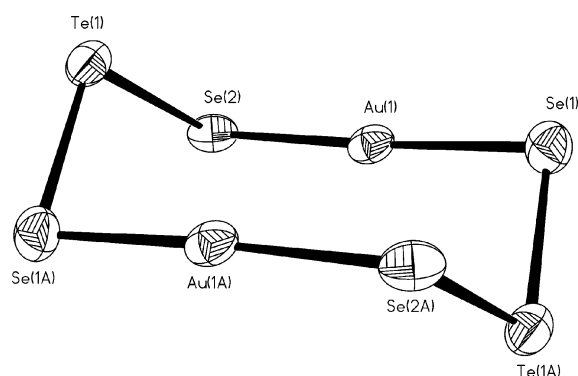


Fig. 1 Drawing of the [Au₂(TeSe₂)₂]²⁻ anion. Selected bond distances (Å) and angles (°): Au(1)–Se(1), 2.402(1); Au(1)–Se(2), 2.407(1); Te(1)–Se(1), 2.493(1); Te(1)–Se(2), 2.487(1); Se(1)–Au(1)–Se(2), 177.41(3); Au(1)–Se(1)–Te(1), 99.64(3); Au(1)–Se(2)–Te(1), 96.66(3); Se(1)–Te(1)–Se(2), 104.71(3). Here and in Fig. 2 displacement ellipsoids are displayed at the 50% probability level.

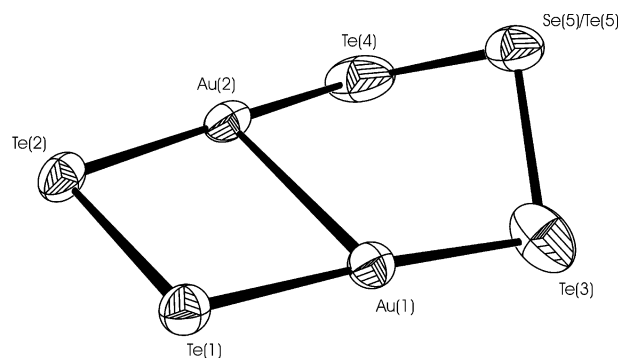


Fig. 2 Drawing of the [Au₂(Te₂)(Te_{2.39}Se_{0.61})]²⁻ anion. Selected bond distances (Å): Au(1)–Au(2), 3.146(1); Au(1)–Te(1), 2.550(1); Au(1)–Te(3), 2.549(1); Au(2)–Te(4), 2.539(2); Au(2)–Te(2), 2.562(1); Te(1)–Te(2), 2.765(1); Te(3)–Se(5)/Te(5), 2.597(2); Te(4)–Se(5)/Te(5), 2.554(2). The latter two distances are non-representative owing to the 0.39/0.61 Te/Se disorder at position 5.

reaction, as opposed to the one that occurs in the absence of PEt₃, the [TeSe₂]²⁻ anion has not remained intact but rather from its disintegration the η²-attachment to the Au centers of both Te₃ and TeSeTe groups has resulted. The resultant anions are not very stable in the reaction solution and transform to the more stable compound [PPh₄]₂[Au₂(Te₂)₂],^{19,20} presumably through the extraction of the apical Q atom with PEt₃ with concomitant formation of a Te–Te single bond.

Notes and references

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- 11 $\text{Na}_2[\text{TeSe}_3]$ was prepared by reaction of stoichiometric amounts of the elements in NH_3 (liq). A signal at $\delta = 437.6$ ppm in the ^{77}Se NMR spectrum of this compound in DMF at -40°C compares well with that of 468 ppm obtained for $[\text{K}(2,2,2\text{-crypt})]_2[\text{TeSe}_3]$ in ethylenediamine.²¹ At room temperature to 5 mL of a DMF solution of 100 mg (0.24 mmol) of $\text{Na}_2[\text{TeSe}_3]$ was slowly added 5 mL of a DMF solution of 53.5 mg (0.24 mmol) of AuCN and 0.1 mL of PEt_3 . The solution was stirred for 2 h and then 100 mg of solid PPh_4Br was added. The resulting mixture was stirred for another 2 h and then filtered. The brown filtrate was layered with 10 mL of ether to produce brown crystalline blocks of $[\text{PPh}_4]_2[\text{Au}_2(\text{TeSe}_2)_2]$ in 33% yield based on AuCN. Anal: $\text{C}_{48}\text{H}_{40}\text{Au}_2\text{P}_2\text{Se}_4\text{Te}_2$: C, 35.07%, H, 2.45%. Found: C, 35.12%, H, 2.36%. ^{77}Se NMR (DMF): $T = 50^\circ\text{C}$, $\delta = 28$ ppm; $T = 23^\circ\text{C}$, $\delta = 25$ ppm; $T = -40^\circ\text{C}$, $\delta = 15$ ppm. UV-Vis (DMF, 25°C): maximum ≈ 300 nm; shoulder ≈ 400 nm.
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- 15 $[\text{PPh}_4]_2[\text{Au}_2(\text{TeSe}_2)_2]$: brown prisms, $\text{C}_{48}\text{H}_{40}\text{Au}_2\text{P}_2\text{Se}_4\text{Te}_2$, $M_r = 1643.71$, monoclinic, space group $P2_1/n$, $a = 9.8089(5)$, $b = 13.6406(7)$, $c = 17.5009(1)$ Å, $\beta = 97.751(1)^\circ$, $V = 2320.2(2)$ Å³, $T = 153$ K, $Z = 2$, $\rho_{\text{calcd}} = 2.353$ g cm⁻³, $\mu = 107.88$ cm⁻¹, $2\theta_{\text{max}} = 46.52^\circ$, 19346 reflections measured, 3331 independent reflections, 262 refined parameters and 0 restraints, $R_1 = 0.0295$, $wR2 = 0.0855$. Data were collected on a Bruker Smart 1000 CCD diffractometer with MoK α radiation ($\lambda = 0.71073$ Å). Face-indexed absorption corrections were made with the program XPREP.²² The structure was solved by direct methods with the program SHELXS and refined by full-matrix least-squares techniques with the program SHELXL in the SHELXTL-97 suite.²² CCDC 212390. See <http://www.rsc.org/suppdata/cc/b3/b306415h/> for crystallographic data in .cif or other electronic format.
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- 18 $[\text{PPh}_4]_2[\text{Au}_2(\text{Te}_2)(\text{Te}_{2.39}\text{Se}_{0.61})]$: brown blocks, $\text{C}_{48}\text{H}_{40}\text{Au}_2\text{P}_2\text{Se}_{0.61}\text{Te}_{4.39}$, $M_r = 1681.00$, triclinic, space group $P\bar{1}$, $a = 10.591(3)$, $b = 11.161(3)$, $c = 21.245(5)$ Å, $\alpha = 104.928(4)^\circ$, $\beta = 95.396(4)^\circ$, $\gamma = 98.466(4)^\circ$, $V = 2377(1)$ Å³, $T = 153$ K, $Z = 2$, $\rho_{\text{calcd}} = 2.349$ g cm⁻³, $\mu = 93.77$ cm⁻¹, $2\theta_{\text{max}} = 46.58^\circ$, 19937 reflections measured, 6844 independent reflections, 515 refined parameters and 0 restraints, $R_1 = 0.0601$, $wR2 = 0.1848$. CCDC 212391. See <http://www.rsc.org/suppdata/cc/b3/b306415h/> for crystallographic data in .cif or other electronic format.
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- 20 $[\text{PPh}_4]_2[\text{Au}_2(\text{Te}_2)_2]$: brown blocks, $\text{C}_{48}\text{H}_{40}\text{Au}_2\text{P}_2\text{Te}_4$, $M_r = 1583.07$, triclinic, space group $P\bar{1}$, $a = 10.498(1)$, $b = 10.526(1)$, $c = 11.153(1)$ Å, $\alpha = 81.459(2)^\circ$, $\beta = 77.221(2)^\circ$, $\gamma = 72.994(2)^\circ$, $V = 1144.7(2)$ Å³, $T = 153$ K, $Z = 1$, $\rho_{\text{calcd}} = 2.296$ g cm⁻³, $\mu = 90.01$ cm⁻¹, $2\theta_{\text{max}} = 57.50^\circ$, 13840 reflections measured, 5450 independent reflections, 253 refined parameters and 0 restraints, $R_1 = 0.0265$, $wR2 = 0.0703$. This structure determination is more precise than an earlier one of the same salt¹⁹ and of the PNP⁺ salt.²³ CCDC 212389. See <http://www.rsc.org/suppdata/cc/b3/b306415h/> for crystallographic data in .cif or other electronic format.
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