Inorg. Chem. **2004**, *43*, 5436–5441

Inorganic Chemistry
Article

Syntheses and Characterization of Some Mixed Te/Se Polychalcogenide Anions $[Te_mSe_n]^{2-}$

Perumal Sekar and James A. Ibers*

Department of Chemistry, Northwestern University, 2145 Sheridan Road,
Evanston, Illinois 60208-3113

Received February 18, 2004

Several mixed Te/Se polychalcogenide anions $[Te_mSe_n]^{2-}$ were synthesized at 293 K by reactions between Te_n^{2-} and Se_n^{2-} anions in *N*,*N*-dimethylformamide (DMF) in the presence of different-size ammonium or phosphonium cations, in some cases in the presence of metal species. The structures of these anions were determined by single-crystal X-ray diffraction methods. The crystal structures of $[NEt_4]_2[Te_3Se_6]$ (**1**) and $[NEt_4]_2[Te_3Se_7]$ (**2**) consist, respectively, of one-dimensional infinite ${}^1_\infty[Te_3Se_6{}^{2-}]$ and ${}^1_\infty[Te_3Se_7{}^{2-}]$ anionic chains separated by NEt_4^+ cations. In compound **1**, each chain comprises Te_3Se_5 eight-membered rings bridged by Se atoms. The Te_3Se_5 ring has an "open book" conformation. The NMR spectrum of a DMF solution of $[NEt_4]_2[Te_3Se_6]$ crystals at 223 K shows ^{77}Se resonances at $\delta = 290$, 349, and 771 ppm and a single ^{125}Te resonance at $\delta = 944.7$ ppm. In compound **2**, each chain comprises Te_3Se_6 five- and six-membered rings bridged by Se atoms. The Te_3Se_6 ring can be regarded as an inorganic analogue of bicyclononane. The anion of $[PPh_4]_2[Te_2Se_2]$ (**4**) contains a Se–Te–Te–Se chain with the terminal Se atoms trans to one another. The new compounds $[PPN]_2[TeSe_{10}]$ (**3**), $[NMe_4]_2[TeSe_3]\cdot DMF$ (**5**), and $[NEt_4]_2[TeSe_3]$ (**6**) contain known anions.

Introduction

Although many polytelluride and polyselenide anions have been isolated and their structures characterized by single-crystal X-ray difffraction methods,[1−10] the known mixed Te/Se polychalcogenide anions $[Te_mSe_n]^{p-}$ are limited to $[TeSe_2]^{2-}$,[11] $[TeSe_3]^{2-}$,[11,12] $[Te(Se_5)_2]^{2-}$,[13] $[Te(Se_5)_3]^{4-}$,[14] and $[\{Te(Se_2)\}_2(\mu_2\text{-}(Se_2))]^{2-}$.[14] These anions, which have been prepared by high-temperature solid-state or solventothermal or solution methods, contain Te^{II} or Te^{IV} centers bonded to Se_n^{2-} species ($n = 1$, 2, or 5). We recently reported the compound $[PPh_4]_2[NEt_4][CuTe_7]$, which was synthesized from the reaction in DMF of CuCl with a polytelluride solution.[15] A novel mixed Te/Se anion $[Te_3Se_7]^{2-}$ containing five- and six-membered rings was isolated when we attempted the synthesis of a hypothetical mixed $[CuTe_{7-n}Se_n]^{3-}$ anion by addition of polyselenide to the reaction that afforded $[CuTe_7]^{3-}$. Also two other mixed Te/Se anions were isolated from reactions of other metal sources such as $HgCl_2$ and $Cr(CO)_6$ with polytelluride/polyselenide solutions in DMF. We therefore decided to study the reactions of polyselenide and polytelluride anions with one another in the presence of different-size cations, in some instances in the presence of metal sources. Here, we report the syntheses by such reactions of six new mixed Te/Se compounds. Three of these

---

* To whom correspondence should be addressed. E-mail: ibers@chem.northwestern.edu.

(1) Brese, N. E.; Randall, C. R.; Ibers, J. A. *Inorg. Chem.* **1988**, *27*, 940−943.
(2) Sheldrick, W. S.; Braunbeck, H. G. *Z. Naturforsch. B: Anorg. Chem. Org. Chem.* **1989**, *44*, 1397−1401.
(3) Fenske, D.; Kräuter, G.; Dehnicke, K. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 390−391.
(4) Müller, V.; Dehnicke, K.; Fenske, D.; Baum, G. *Z. Naturforsch. B: Chem. Sci.* **1991**, *46*, 63−67.
(5) Staffel, R.; Müller, U.; Ahle, A.; Dehnicke, K. *Z. Naturforsch. B: Chem. Sci.* **1991**, *46*, 1287−1292.
(6) Krebs, B.; Lührs, E.; Willmer, R.; Ahlers, F.-P. *Z. Anorg. Allg. Chem.* **1991**, *592*, 17−34.
(7) Huang, S.-P.; Dhingra, S.; Kanatzidis, M. G. *Polyhedron* **1992**, *11*, 1869−1875.
(8) Müller, V.; Grebe, C.; Müller, U.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1993**, *619*, 416−420.
(9) Müller, V.; Ahle, A.; Frenzen, G.; Neumüller, B.; Dehnicke, K.; Fenske, D. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1247−1256.
(10) Smith, D. M.; Ibers, J. A. *Coord. Chem. Rev.* **2000**, *200−202*, 187−205.
(11) Björgvinsson, M.; Sawyer, J. F.; Schrobilgen, G. J. *Inorg. Chem.* **1991**, *30*, 4238−4245.
(12) Zagler, R.; Eisenmann, B. *Z. Kristallogr.* **1988**, *183*, 193−200.
(13) Zagler, R.; Eisenmann, B. *Z. Naturforsch. B: Chem. Sci.* **1991**, *46*, 593−601.
(14) Wachhold, M.; Sheldrick, W. S. *J. Solid State Chem.* **1997**, *134*, 364−375.
(15) Sekar, P.; Arnold, F. P., Jr.; Ibers, J. A. *Inorg. Chem.* **2002**, *41*, 577−581.

10.1021/ic040026h CCC: $27.50

contain previously unknown $[Te_mSe_n]^{2-}$ anions; among these anions, two comprise infinite chains of Te/Se rings.

Experimental Section

General Procedures. All manipulations were performed under an inert atmosphere of N_2 with the use of standard Schlenk-line techniques or under Ar in a glovebox. Solvents were dried, distilled, and degassed under N_2 before use. Anhydrous *N*,*N*-dimethylformamide (DMF), purchased from Fisher Chemical, Fair Lawn, NJ, was stored over activated molecular sieves and degassed with dry N_2 before use. Anhydrous diethyl ether (Et_2O) and tetrahydrofuran (THF) were distilled from Na and benzophenone. Compounds Li_2Q (Q = Se, Te) were prepared from the stoichiometric reactions of Li and Q in liquid NH_3. CuCl (Strem Chemical Co., Newburyport, MA), $Cr(CO)_6$ (Pressure Chemical Co., Pittsburgh, PA), and PEt_3 (Aldrich Chemical Co., Milwaukee, WI) were used as received. Energy-dispersive analyses by X-ray (EDAX) were performed with the use of a Hitachi 3500 scanning electron microscope equipped with an X-ray detector. ^{77}Se and ^{125}Te NMR spectra were recorded on an INOVA 400-MHz spectrometer with a 10-mm broadband NMR probe with DMF-d_7/DMF as the solvent. ^{77}Se chemical shifts, in ppm, were recorded at 76.287 MHz and referenced to an external standard of a saturated solution of Ph_2Se_2 in CD_2Cl_2 (set to 460 ppm). ^{125}Te chemical shifts, in ppm, were recorded at 126.234 MHz and referenced to an external standard of a saturated solution of Ph_2Te_2 in CD_2Cl_2 (set to 422 ppm). Electrospray mass spectra were obtained on a Micromass Quattro II instrument. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

Synthesis of $[NEt_4]_2[Te_3Se_6]$ (1). Li_2Se (0.217 g, 2.34 mmol), Se (0.552 g, 6.99 mmol), Li_2Te (0.142 g, 1.00 mmol), Te (0.383 g, 3.00 mmol), and NEt_4Cl (0.331 g, 2.00 mmol) were dissolved in DMF (20 mL). The resulting yellow-green solution was stirred at 293 K for 2 h, filtered, and then layered with Et_2O (10 mL). Black crystals of $[NEt_4]_2[Te_3Se_6]$ grew overnight at 293 K. Yield: 850 mg, 0.76 mmol, 76% (based on NEt_4Cl). ^{77}Se NMR (400 MHz, DMF, 223 K, Ph_2Se_2): $\delta = 290, 349, 771$ ppm. ^{125}Te NMR (400 MHz, DMF, 223 K, Ph_2Te_2): $\delta = 944.7$ ppm. ESI-MS (DMF) *m/z* (%): 494 (70) $[M^+ - 4Se]$, 288 (24) $[M^+ - 5Se + Te]$, 238 (20) $[M^+ - 4Se + 2Te]$. Anal. Calcd for $C_{16}H_{40}N_2Se_6Te_3$: C 17.20, H 3.61, N 2.51%. Found: C 17.13, H 3.43, N 2.41%.

Synthesis of $[NEt_4]_2[Te_3Se_7]$ (2). Li_2Se (0.217 g, 2.34 mmol), Se (0.552 g, 6.99 mmol), Li_2Te (0.142 g, 1.00 mmol), Te (0.383 g, 3.00 mmol), CuCl (0.099 g, 1 mmol), PEt_3 (0.2 mL), NEt_4Cl (0.166 g, 1.00 mmol), and PPh_4Br (0.419 g, 1.00 mmol) were dissolved in DMF (20 mL). Black needles of $[NEt_4]_2[Te_3Se_7]$ grew over a few weeks at 278 K. Yield: 0.2 g, 0.17 mmol, 33% (based on NEt_4Cl). The synthesis could not be repeated successfully, either from the above reaction or with the addition of PPh_4Br to the reaction system that afforded compound **1**.

Synthesis of $[PPN]_2[TeSe_{10}]$ (3). Compound **3** was synthesized in a manner similar to the synthesis of compound **1**, but with the substitution of [PPN]Cl (PPN = bis(triphenylphosphine)iminium) (1.148 g, 2.00 mmol) for NEt_4Cl. When the solution was layered with Et_2O (10 mL), black crystals of $[PPN]_2[TeSe_{10}]$ grew overnight at 293 K. Layering additional Et_2O (10 mL) to the parent solution gave a second batch of $[PPN]_2[TeSe_{10}]$ crystals. Total yield: 1.27 g, 0.64 mmol, 64% (based on [PPN]Cl). Anal. Calcd for $C_{72}H_{60}N_2P_4Se_{10}Te$: C 43.36, H 3.03, N 1.40%. Found: C 43.60, H 3.08, N 1.34%.

Synthesis of $[PPh_4]_2[Te_2Se_2]$ (4). Li_2Se (0.217 g, 2.34 mmol), Se (0.552 g, 6.99 mmol), Li_2Te (0.142 g, 1.00 mmol), Te (0.383 g, 3.00 mmol), $Cr(CO)_6$ (0.220 g, 1 mmol), and PPh_4Br (0.838 g, 2.00 mmol) were dissolved in DMF (20 mL). The reaction mixture was stirred at 293 K for 3 days. Only few black crystals of $[PPh_4]_2[Te_2Se_2]$ formed after the solution was layered with Et_2O (10 mL) at 293 K. Attempts to isolate compound **4** without $Cr(CO)_6$ in the reaction mixture afforded the known compound $[PPh_4]_2[TeSe_{10}]$,[7] as deduced from a crystal-structure determination. (Details can be found in the Supporting Information.) The yield of $[PPh_4]_2[TeSe_{10}]$ was 1.06 g, 0.66 mmol, 66% (based on PPh_4Br).

Synthesis of $[NMe_4]_2[TeSe_3]\cdot DMF$ (5). Li_2Se (0.217 g, 2.34 mmol), Se (0.552 g, 6.99 mmol), Li_2Te (0.142 g, 1.00 mmol), Te (0.383 g, 3.00 mmol), and NMe_4Cl (0.219 g, 2.00 mmol) were dissolved in DMF (20 mL). Red crystals of $[NMe_4]_2[TeSe_3]\cdot DMF$ grew overnight at 293 K. Yield: 0.382 g, 0.65 mmol, 65% (based on NMe_4Cl). Anal. Calcd for $C_{11}H_{31}N_3OSe_3Te$: C 22.55, H 5.33, N 7.17%. Found: C 22.63, H 4.96, N 7.31%.

Synthesis of $[NEt_4]_2[TeSe_3]$ (6). Li_2Se (0.217 g, 2.34 mmol), Se (0.552 g, 6.99 mmol), Li_2Te (0.142 g, 1.00 mmol), Te (0.383 g, 3.00 mmol), NEt_4Cl (0.166 g, 1.00 mmol), and PPh_4Br (0.419 g, 1.00 mmol) were dissolved in DMF (20 mL). Red crystals of $[NEt_4]_2[TeSe_3]$ grew overnight at 293 K. Yield: 0.437 g, 0.70 mmol, 70% (based on NEt_4Cl). ^{77}Se NMR (400 MHz, DMF, 223 K, Ph_2Se_2): $\delta = 477$ ppm. ^{125}Te NMR (400 MHz, DMF, 223 K, Ph_2Te_2): $\delta = 1088$ ppm. Anal. Calcd for $C_{16}H_{40}N_2Se_3Te$: C 30.75, H 6.45, N 4.48%. Found: C 30.83, H 6.63, N 4.54%.

Crystallography. Single-crystal X-ray diffraction data were collected with the use of the program SMART[16] on a Bruker Smart 1000 CCD diffractometer[16] at 153 K with monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). The diffracted intensities generated by a scan of 0.3° in ω were recorded on four sets of 606 frames at φ settings of 0°, 90°, 180°, and 270°, with an additional 50 frames at $\varphi = 0°$. The exposure times (s/frame) were 10 (for **4** and **6**), 15 (for **1**, **3**, and **5**), and 20 (for **2**). Cell refinement and data reduction were carried out with the use of the program SAINT.[16] There was no evidence of twinning in any of the data sets. Face-indexed absorption corrections were made with the program XPREP.[17] Then the program SADABS was employed to make incident beam and decay corrections.[16] The structures were 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.[17] Hydrogen atoms were generated in calculated positions and constrained with the use of a riding model. The final models involved anisotropic displacement parameters for all non-hydrogen atoms. Except in the following instances, such refinements were straightforward. For compound **1**, there is Te/Se disorder at one position, as judged both by bond distances and by refinement the Te/Se occupancy, which converged to 0.53(4) and was subsequently set to 0.50. There are two independent NEt_4^+ cations in the asymmetric unit, each lying on a mirror plane. The independent atoms in these cations were refined with a series of restraints. Compound **4** has two independent $[Te_2Se_2]^{2-}$ anions and four PPh_4^+ cations in the asymmetric unit. One of these anions is disordered and could not be modeled in a totally satisfactory manner; atom Te3 from the second $[Te_2Se_2]^{2-}$ anion occupies two different sites in approximately a 0.62(1):0.38(1) manner.

Selected crystallographic data for compounds **1**−**6** are listed in Table 1. Further crystallographic details can be found in the Supporting Information.

---

(16) Bruker. SMART Version 5.054 Data Collection and SAINT-Plus Version 6.45 Data Processing Software for the SMART System; Bruker Analytical X-ray Instruments, Inc., Madison, WI, 2003.

(17) Sheldrick, G. M. SHELXTL DOS/Windows/NT Version 6.14; Bruker Analytical X-ray Instruments, Inc., Madison, WI, 2003.

Table 1. Selected Crystallographic Data

	$[NEt_4]_2[Te_3Se_6]$ (**1**)	$[NEt_4]_2[Te_3Se_7]$ (**2**)	$[PPN]_2[TeSe_{10}]$ (**3**)	$[PPh_4]_2[Te_2Se_2]$ (**4**)	$[NMe_4]_2[TeSe_3]\cdot DMF$ (**5**)	$[NEt_4]_2[TeSe_3]$ (**6**)
formula	$C_{16}H_{40}N_2Se_6Te_3$	$C_{16}H_{40}N_2Se_7Te_3$	$C_{72}H_{60}N_2P_4Se_{10}Te$	$C_{96}H_{80}P_4Se_4Te_4$	$C_{11}H_{31}N_3OSe_3Te$	$C_{16}H_{40}N_2Se_3Te$
fw	1117.06	1196.02	1994.30	2183.72	585.87	624.98
space group	*Pnma*	*Pbca*	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a (Å)	14.4975(8)	14.811(5)	11.0540(8)	11.346(1)	15.601(1)	8.5056(7)
b (Å)	13.1068(7)	12.795(4)	18.427(1)	19.420(2)	11.7941(8)	13.467(1)
c (Å)	15.8270(8)	32.802(11)	17.844(1)	20.000(3)	11.8795(8)	20.889(2)
α (deg)	90	90	90	89.402(2)	90	
β (deg)	90	90	95.441(1)	76.282(2)	107.992(1)	97.097(1)
γ (deg)	90	90	90	88.457(2)	90	
V (Å^3)	3007.4(3)	6216(3)	3618.3(5)	4279.3(9)	2079.0(2)	2374.5(3)
Z	4	8	2	2	4	4
T (K)	153	153	153	153	153	153
ρ_{calcd} (g/cm^3)	2.467	2.556	1.830	1.695	1.872	1.748
μ(Mo Kα) (cm^{-1})	101.60	110.03	55.72	31.72	66.82	58.52
$R_1(F)^a$	0.024	0.065	0.059	0.086	0.029	0.026
$R_w(F^2)^b$	0.060	0.208	0.199	0.254	0.071	0.070

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F_o^2) = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (qF_o^2)^2$ for $F_o^2 > 0$; $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 \leq 0$; $q = 0.03$ for **1**, **5**, and **6**; $q = 0.1$ for **2**, **3**, and **4**.

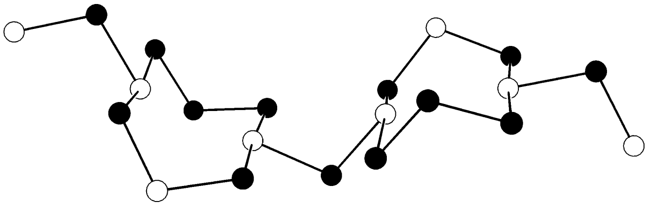

Figure 1. Sketch of part of the infinite chain of the ${}^{1}_{\infty}[Te_3Se_6{}^{2-}]$ anion in $[NEt_4]_2[Te_3Se_6]$ (**1**). The black circles are Se; the white circles are Te. The disorder, which presumably results from the random "flipping" of the Te_3Se_5 rings, is not shown.

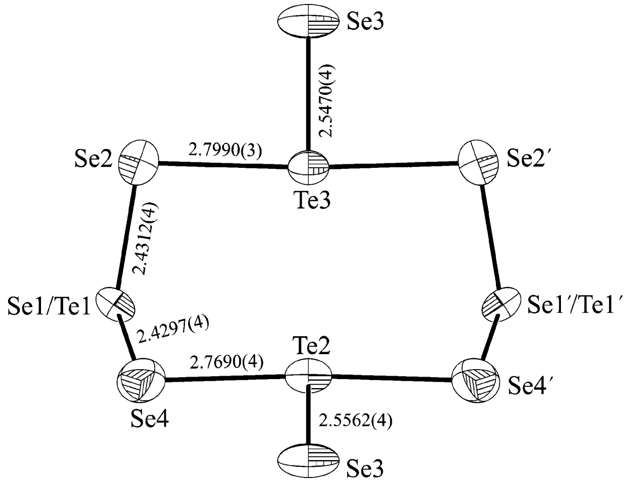

Figure 2. Te_3Se_5 ring in $[NEt_4]_2[Te_3Se_6]$ (**1**). Primed atoms are related to the corresponding unprimed atoms by the mirror plane through atoms Se3, Te3, and Te2. Displacement ellipsoids are drawn at the 75% probability level. Bond distances are shown. Bond angles are Se3−Te3−Se2, 88.24(1)°; Se2−Te3−Se2′, 176.43(1)°; Se3−Te2−Se4, 84.22(1)°; Se4−Te2−Se4′, 167.89(2)°; Se4−Se1/Te1−Se2, 106.99(1)°; Se1/Te1−Se2−Te3, 97.48(1)°; Te3−Se3−Te2, 104.67(2)°; Se1/Te1−Se4−Te2, 94.36(1)°.

Results

Syntheses. Six new mixed Te/Se compounds (**1**−**6**) resulted from reactions at 293 K of $Te_n{}^{2-}$and $Se_n{}^{2-}$ anions in *N*,*N*-dimethylformamide (DMF) in the presence of different-size ammonium or phosphonium cations and, in some instances, the presence of metal sources. With the exception of compound **2**, the syntheses are reproducible; the yields are good except for that of compound **4**. Three of these compounds contain previously unknown $[Te_mSe_n]^{2-}$ anions. The compounds are readily soluble in DMF to afford very air-sensitive solutions. However, crystals of these materials are modestly air stable.

Structure of $[NEt_4]_2[Te_3Se_6]$ (1). The crystal structure of $[NEt_4]_2[Te_3Se_6]$ consists of one-dimensional infinite ${}^{1}_{\infty}[Te_3Se_6{}^{2-}]$ anionic chains separated by $NEt_4{}^+$ cations. Each chain comprises Te_3Se_5 eight-membered rings bridged by Se atoms (Figure 1). There is a crystallographically imposed mirror plane passing through atoms Se3, Te2, and Te3. From the refinement of the X-ray data, the 1 position is occupied 50% by Se1 and 50% by Te1 (Figure 2). This disorder results from the random "flipping" of the Te_3Se_6 rings along the chain and not from cocrystallization of the hypothetical species $[NEt_4]_2[Te_2Se_7]$ and $[NEt_4]_2[Te_4Se_5]$, because such cocrystallization would not be expected to comprise 50% of each species. The Te3, Se2, Se2′, Te2, Se4, Se4′ portion of the Te_3Se_5 ring is essentially planar (mean deviation, 0.055 Å), with atoms Se1 and Te1 1.35 Å from this plane. Thus, the Te_3Se_5 ring can be regarded as having an "open book" conformation. The eight-membered rings in the chain alternate in their orientation (Figure 1).

Bond distances and angles are shown in Figure 2. The Te−Se distances not affected by disorder are typical of Te−Se single bonds, for example, 2.501(1) Å in $[TeSe_2]^{2-}$.[11] The (Se1/Te1)−Se2 and (Se1/Te1)−Se4 bond lengths at 2.43 Å are a superposition of such a Te−Se single bond with a Se−Se single bond (typically, about 2.34 Å in length).

$[NEt_4]_2[Te_3Se_6]$ is diamagnetic in the range 5−300 K. The ^{77}Se NMR spectrum of a DMF solution of $[NEt_4]_2[Te_3Se_6]$ crystals at 223 K shows resonances at $\delta = 290$, 349, and 771 ppm, and the ^{125}Te NMR spectrum of the same solution shows a single resonance at $\delta = 944.7$ ppm. From the solid-state structure (Figure 1), three ^{77}Se and two ^{125}Te resonances are expected. However, it is improbable that the infinite chain persists in solution. The ^{77}Se resonances fall in the same region as those reported for the $[TeSe_3]^{2-}$,[11,18] $[MTe_nSe_{8-n}]^{2-}$ (M = Zn, Cd, Hg; $n = 0$−4),[19] and $[Se_n]^{2-}$ ($n = 2$−6)[18,20]

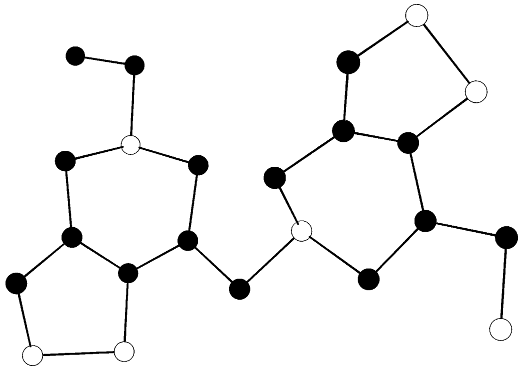

Figure 3. Sketch of part of the infinite chain of the $^{1}_{\infty}[Te_3Se_7{}^{2-}]$ anion in $[NEt_4]_2[Te_3Se_7]$ (**2**). The black circles are Se; the white circles are Te.

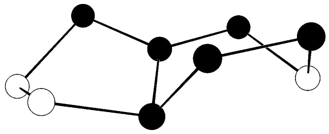

Figure 4. Sketch of the fused rings in $[NEt_4]_2[Te_3Se_7]$ (**2**). The black circles are Se; the white circles are Te.

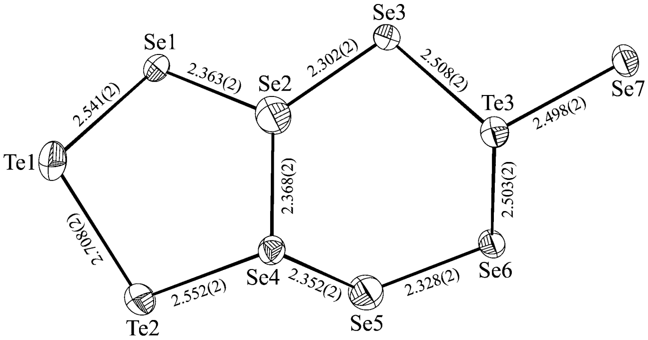

Figure 5. Te_3Se_6 ring in $[NEt_4]_2[Te_3Se_7]$ (**2**). Displacement ellipsoids are drawn at the 50% probability level. Bond distances are shown, except for Se5−Se7′ = 2.345(2) Å. Bond angles are Se1−Te1−Te2, 99.54(6)°; Se1−Se2−Se3, 120.59(9)°; Se1−Se2−Se4, 118.22(9)°; Se2−Se1−Te1, 97.17(8)°; Se2−Se3−Te3, 100.77(7)°; Se2−Se4−Te2, 100.21(7)°; Se2−Se4−Se5, 94.53(8)°; Se3−Se2−Se4, 121.13(9)°; Se3−Te3−Se6, 106.20(6)°; Se3−Te3−Se7, 103.05(6)°; Se4−Te2−Te1, 95.67(5)°; Se4−Se5−Se6, 119.70(8)°; Se5−Se4−Te2, 102.93(7)°; Se5−Se6−Te3, 101.44(7)°; Se6−Te3−Se7, 101.28(6)°.

anions. The observed ^{125}Te NMR resonance at $\delta = 944.7$ ppm compares favorably with that of $\delta = 1087$ ppm for the $[TeSe_3]^{2-}$ anion.[11]

Structure of $[NEt_4]_2[Te_3Se_7]$ (2). The crystal structure of $[NEt_4]_2[Te_3Se_7]$ consists of one-dimensional infinite $^{1}_{\infty}[Te_3Se_7{}^{2-}]$ anionic chains separated by $NEt_4{}^+$ cations. Each chain comprises fused five- and six-membered rings of composition Te_3Se_6 bridged by Se atoms (Figure 3). These rings alternate in their orientation along the chain. The Te_3Se_6 ring (Figure 4) can be regarded as an inorganic analogue of bicyclononane. The bridging Se atom in the chain is bonded to a Te atom of the six-membered ring and a Se atom of the six-membered ring from the next repeating unit. Bond distances and angles are shown in Figure 5. The Se−Se, Se−Te, and Te−Te bond distances are typical of single bonds. This is the first example of a structure of a mixed Se/Te compound containing fused five- and six-membered rings.

Structure of $[PPN]_2[TeSe_{10}]$ (3). The crystal structure of **3** contains a $[TeSe_{10}]^{2-}$ anion. This anion has been reported previously in $[K(2,2,2\text{-crypt})]_2[TeSe_{10}]$,[13] $[Ba(2,2,2\text{-crypt})(en)][TeSe_{10}]\cdot en_{0.5}$,[13] and $[PPh_4]_2[TeSe_{10}]$.[7] The structure of $[TeSe_{10}]^{2-}$ anion consists of two similar $[Se_5]^{2-}$ chains coordinated to a Te^{II} center in a square-planar geometry to form a spirocyclic ring. The $[TeSe_{10}]^{2-}$ anion possesses a crystallographically imposed inversion symmetry. The Te−Se bond distances (Table 2) are longer than the typical Te−Se single bond distance (2.53 Å),[21] but comparable to those in the related $[TeSe_{10}]^{2-}$ anions.[13]

Structure of $[PPh_4]_2[Te_2Se_2]$ (4). The crystal structure of **4** contains a Se−Te−Te−Se chain with the terminal Se atoms trans to one another. This anion is analogous to the homopolychalcogenide anions $Se_4{}^{2-}$ and $Te_4{}^{2-}$. The two independent $[Te_2Se_2]^{2-}$ anions in the unit cell are shown in Figure 6. The $[Te_2Se_2]^{2-}$ anion has been proposed as one of the intermediates in the scheme of converting a polytelluride solution and elemental Se into $[TeSe_3]^{2-}$.[12,18] ^{77}Se and ^{125}Te NMR data have been reported for this anion.[18]

Structures of $[NMe_4]_2[TeSe_3]\cdot DMF$ (5) and $[NEt_4]_2[TeSe_3]$ (6). The crystal structures of **5** and **6** contain the trigonal-pyramidal $[TeSe_3]^{2-}$ anion. The Te−Se bond distances (Table 3) are shorter than a typical Te−Se single bond distance (2.53 Å),[21] but comparable to those in related salts containing the $[TeSe_3]^{2-}$ anion.[11] The ^{77}Se ($\delta = 477$ ppm) and ^{125}Te ($\delta = 1088$ ppm) NMR resonances of **6** at 223 K are very close to the reported value for $[K(2,2,2\text{-crypt})]_2[TeSe_3]$[11] (^{77}Se ($\delta = 468$ ppm) and ^{125}Te ($\delta = 1087$ ppm)).

Discussion

From crystallographic studies, rings of the Q_8 type are well-known for Q = S and Se, but are very rare for Q = Te. Te_8 rings are found in Cs_3Te_{22} [22] and Cs_4Te_{28}.[23] From spectroscopic studies, eight-membered rings of the Q_8 type are known for S/Se,[24−27] S/Te,[28] and 1,2-$TeSeS_6$.[28] Although among the polycations a number of Te/Se ring systems exist,[29] such rings are far less common among the polyanions.[10] For example, the $[Te_8]^{2-}$ anion does not exhibit a ring structure, but rather comprises a Te^{2+} center coordinated in a distorted square-planar fashion to $[Te_4]^{2-}$ and $[Te_3]^{2-}$ chelating rings.[30] Among Te/Se systems, disordered

---

(18) Björgvinsson, M.; Schrobilgen, G. J. *Inorg. Chem.* **1991**, *30*, 2540−2547.

(19) Bollinger, J. C.; Ibers, J. A. *Inorg. Chem.* **1995**, *34*, 1859−1867.

(20) Cusick, J.; Dance, I. *Polyhedron* **1991**, *10*, 2629−2640.

(21) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(22) Sheldrick, W. S.; Wachhold, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 450−451.

(23) Sheldrick, W. S.; Wachhold, M. *J. Chem. Soc., Chem. Commun.* **1996**, 607−608.

(24) Laitinen, R. S.; Pakkanen, T. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1381−1382.

(25) Laitinen, R. S.; Pakkanen, T. A. *Inorg. Chem.* **1987**, *26*, 2598−2603.

(26) Chivers, T.; Laitinen, R. S.; Schmidt, K. J. *Can. J. Chem.* **1992**, *70*, 719−725.

(27) Steudel, R.; Papavassiliou, M.; Baumgart, F. *Z. Naturforsch. B: Chem. Sci.* **1991**, *46*, 1674−1678.

(28) Chivers, T.; Laitinen, R. S.; Schmidt, K. J.; Taavitsainen, J. *Inorg. Chem.* **1993**, *32*, 337−340.

(29) Beck, J. *Coord. Chem. Rev.* **1997**, *163*, 55−70.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **3** and Related Compounds

	$[PPN]_2[TeSe_{10}]$[a] (**3**)	$[K(2,2,2\text{-crypt})]_2[TeSe_{10}]$[b]	$[Ba(2,2,2\text{-crypt})(en)][TeSe_{10}]\cdot en_{0.5}$[b]		$[PPh_4]_2[TeSe_{10}]$[a,c]
			molecule 1	molecule 2	
Te1−Se1	2.809(1)	2.815(2)	2.819(3)	2.805(3)	2.809(2)
Te1−Se5	2.808(1)	2.824(2)	2.823(3)	2.821(3)	2.870(2)
Se1−Se2	2.337(1)	2.305(4)	2.287(6)	2.323(6)	2.348(2)
Se2−Se3	2.377(1)	2.349(4)	2.316(6)	2.341(6)	2.388(3)
Se3−Se4	2.421(1)	2.336(4)	2.309(6)	2.342(6)	2.399(2)
Se4−Se5	2.401(1)	2.311(4)	2.248(6)	2.314(6)	2.347(2)
Te1−Se1−Se2	105.57(3)	104.0(1)	104.2(2)	107.4(2)	99.34(7)
Se1−Se2−Se3	107.62(5)	107.2(1)	104.1(2)	106.6(2)	103.93(7)
Se2−Se3−Se4	103.33(4)	103.2(1)	100.2(2)	102.8(2)	104.88(10)
Se3−Se4−Se5	104.00(5)	106.1(1)	106.1(2)	107.3(2)	106.72(10)
Se4−Se5−Te1	103.95(3)	105.2(1)	108.8(2)	104.0(2)	109.95(8)
Se5−Te1−Se1	93.03(3)	95.6(1)	106.8(2)	105.3(2)	93.39(5)
Se5′−Te1−Se1	86.97(3)	84.4(1)	73.2(2)	74.7(2)	86.62(5)

[a] This work. [b] Reference 13. [c] For this compound, ref 7 reports the synthesis and limited crystallographic characterization from X-ray powder diffraction data.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **5**, **6**, and Related Compounds

	$[NMe_4]_2[TeSe_3]\cdot DMF$[a] (**5**)	$[NEt_4]_2[TeSe_3]$[a] (**6**)	Na_2TeSe_3[b]	K_2TeSe_3[b]	$[K(2,2,2\text{-crypt})]_2[TeSe_3]$[c]
Te1−Se1	2.4724(4)	2.4822(3)	2.515(2)	2.500(4)	2.454(4)
Te1−Se2	2.4598(4)	2.4767(3)	2.499(2)	2.496(4)	2.465(4)
Te1−Se3	2.4853(4)	2.4714(4)	2.494(2)	2.478(4)	2.460(4)
Se1−Te1−Se2	105.74(1)	105.01(1)	100.4(1)	102.6(1)	108.9(1)
Se1−Te1−Se3	105.25(1)	106.47(1)	102.0(1)	105.6(1)	104.8(2)
Se2−Te1−Se3	105.65(1)	106.93(1)	102.9(1)	101.9(1)	107.4(1)

[a] This work. [b] Reference 12. [c] Reference 11.

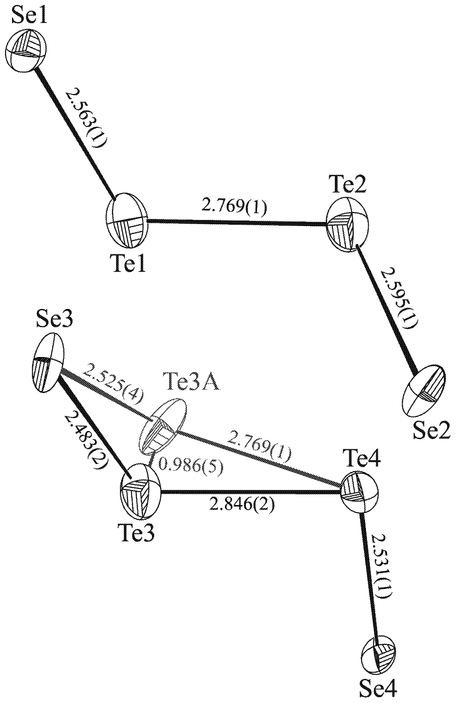

Figure 6. Structure of the ordered (top) and disordered (bottom) $[Te_2Se_2]^{2-}$ anions in $[PPh_4]_2[Te_2Se_2]$ (**4**). Displacement ellipsoids are drawn at the 50% (top) and 30% (bottom) probability levels. Bond distances are shown, but are not representative for the disordered anion in which Te3/Te3A = 0.62:0.38. Bond angles for the ordered anion are Se1−Te1−Te2, 113.52(3)°; Se2−Te2−Te1, 109.12(3)°.

$Te_{0.32}Se_{7.68}$[31] and $Te_{1.05}Se_{5.95}$[32] rings have been claimed, and the Te_4Se_2[33] ring has been reported. An ordered Te_3Se_3 ring is found in $Cs_4Te_{9.74}Se_{13.26}$.[14] The structure of Rb_2TeSe_4,[34] determined from X-ray powder data, is believed to contain an infinite chain of Te_2Se_4 six-membered rings sharing Te centers. Thus, the Te_3Se_5 ring found in $[NEt_4]_2[Te_3Se_6]$ (**1**) and the fused five- and six-membered rings of composition Te_3Se_6 found in $[NEt_4]_2[Te_3Se_7]$ (**2**) are further examples of mixed Te/Se rings.

Complex equilibria among multiple species are typical of polytelluride and polyselenide solutions.[18,20,35−41] The mixed polytelluride/polyselenide solution in the present preparation is no exception and probably displays even more complex equilibria among Se_n^{2-}, Te_n^{2-}, and $[Te_mSe_n]^{2-}$ species. Indeed, in the presence of NEt_4^+, $[NEt_4]_2[Te_3Se_6]$ (**1**) is isolated in 76% yield. In contrast, under the same conditions but with a change of cation, we isolate completely different products, including $[PPN]_2[TeSe_{10}]$ (**3**) and $[NMe_4]_2[TeSe_3]\cdot DMF$ (**5**). If the Se/Te ratio is increased from 2.3:1 originally chosen to optimize the yield of **1**, then red Se is produced in these reactions. If the Se/Te ratio is decreased, then Te and Te_4^{2-} are produced. Moreover, the reaction with the

---

(30) Schreiner, B.; Dehnicke, K.; Maczek, K.; Fenske, D. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1414−1418.

(31) Nagata, K.; Hayashi, H.; Miyamoto, Y. *Fukuoka Univ. Sci. Rep.* **1988**, *18*, 21−33.

(32) Nagata, K.; Hayashi, H.; Miyamoto, Y. *Fukuoka Univ. Sci. Rep.* **1988**, *18*, 35−46.

(33) Wachhold, M.; Sheldrick, W. S. *Z. Naturforsch. B: Chem. Sci.* **1997**, *52*, 169−175.

(34) Kretschmann, U.; Böttcher, P. *Z. Naturforsch. B: Anorg. Chem. Org. Chem.* **1985**, *40*, 895−899.

(35) Sharp, K. W.; Koehler, W. H. *Inorg. Chem.* **1977**, *16*, 2258−2265.

(36) Teller, R. G.; Krause, L. J.; Haushalter, R. C. *Inorg. Chem.* **1983**, *22*, 1809−1812.

(37) Schultz, L. D.; Koehler, W. H. *Inorg. Chem.* **1987**, *26*, 1989−1993.

(38) Schultz, L. D. *Inorg. Chim. Acta* **1990**, *176*, 271−275.

(39) Raymond, C. C.; Dick, D. L.; Dorhout, P. K. *Inorg. Chem.* **1997**, *36*, 2678−2681.

(40) Ahrika, A.; Paris, J. *New J. Chem.* **1999**, *23*, 1177−1180.

(41) Ahrika, A.; Robert, J.; Anouti, M.; Paris, J. *New J. Chem.* **2001**, *25*, 741−746.

mixed countercations PPh_4^+ and NEt_4^+, effective for the isolation in high yield of certain $[MTe_7]^{3-}$ species,[15,42,43] produced $[NEt_4]_2[TeSe_3]$ (**6**), a new salt of the known $[TeSe_3]^{2-}$ anion.[11] The presence of a metal species further complicates matters. Thus, $[PPh_4]_2[Te_2Se_2]$ (**4**) could only be synthesized in the presence of $Cr(CO)_6$.

This work demonstrates that new $[Te_mSe_n]^{2-}$ species, some with unprecedented structures, can be isolated reproducibly and in good yield from mixed polytelluride/polyselenide solutions.

Acknowledgment. This work was supported by the U.S. National Science Foundation through Grant CHE9819385. We are indebted to Dr. Regine Herbst-Irmer of the University of Göttingen for her help with the refinement of the disordered NEt_4^+ cations in compound **1**. We thank Dr. Kwasi Mitchell for the magnetic susceptibility measurements.

Supporting Information Available: X-ray crystallographic data in CIF format for $[NEt_4]_2[Te_3Se_6]$ (**1**), $[NEt_4]_2[Te_3Se_7]$ (**2**), $[PPN]_2[TeSe_{10}]$ (**3**), $[PPh_4]_2[Te_2Se_2]$ (**4**), $[NMe_4]_2[TeSe_3]\cdot DMF$ (**5**), $[NEt_4]_2[TeSe_3]$ (**6**), and $[PPh_4]_2[TeSe_{10}]$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC040026H

---

(42) McConnachie, J. M.; Ansari, M. A.; Bollinger, J. C.; Salm, R. J.; Ibers, J. A. *Inorg. Chem.* **1993**, *32*, 3201−3202.

(43) Smith, D. M.; Roof, L. C.; Ansari, M. A.; McConnachie, J. M.; Bollinger, J. C.; Pell, M. A.; Salm, R. J.; Ibers, J. A. *Inorg. Chem.* **1996**, *35*, 4999−5006.