

sintered mixtures of the oxides. In several samples, we have observed resistivities indicative of mixtures of metallic and semiconducting regions that lead to broad superconducting transitions with zero resistance occurring in the region of 10-20 K depending on x . Annealing with O_2 can often improve the conductive properties of such samples.¹⁸

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Articles

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Preparation and Crystal Structures of $(Te_2Se_8)(AsF_6)_2$, $(Te_{4.5}Se_{5.5})(AsF_6)_2$, and $(Te_2Se_6)(Te_2Se_8)(AsF_6)_4(SO_2)_2$

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The preparation of the compounds $(Te_2Se_8)(MF_6)_2$ (**1a**, $M = As$; **1b**, $M = Sb$), $(Te_{4.5}Se_{5.5})(AsF_6)_2$ (**2**), and $(Te_2Se_6)(Te_2Se_8)(AsF_6)_4(SO_2)_2$ (**3**) and the crystal structures of **1a**, **2**, and **3** are reported. Compound **3** contains the cations $Te_2Se_6^{2+}$ and $Te_2Se_8^{2+}$, hexafluoroarsenate anions, and SO_2 solvent molecules. The novel $Te_2Se_6^{2+}$ cation is not isostructural with the previously known cations Se_8^{2+} and S_8^{2+} but instead adopts a bicyclo[2.2.2]octane structure with tellurium atoms in the three-coordinate positions. In both **1a** and **3** the $Te_2Se_8^{2+}$ cations have slightly different dimensions from those observed for the cation in the previously reported compound $(Te_2Se_8)(AsF_6)_2(SO_2)$. Compounds **1a** and **1b** are isomorphous. In **2** the $Te_{4.5}Se_{5.5}^{2+}$ cation is a disordered mixture of $Te_2Se_{10-x}^{2+}$ cations. Some structural relationships between these and related cations are discussed. Crystal data for each compound are as follows: **1a** [**1b**], orthorhombic, $Pbcn$, $a = 16.118$ (3) Å [16.489 (3) Å], $b = 13.098$ (3) Å [13.251 (4) Å], $c = 18.951$ (4) Å [19.422 (6) Å], $V = 4001$ (1) Å³ [4244 (2) Å³]; **2**, orthorhombic, $Pbcn$, $a = 14.790$ (3) Å, $b = 10.783$ (2) Å, $c = 13.304$ (2) Å, $V = 2121.7$ (7) Å³; **3**, monoclinic, $P2_1/c$, $a = 12.432$ (4) Å, $b = 15.956$ (6) Å, $c = 23.053$ (10) Å, $\beta = 96.61$ (3)°, $V = 4542$ (3) Å³.

Introduction

It has been well-established that the pentafluorides AsF_5 and SbF_5 react with sulfur, selenium, or tellurium in SO_2 solution to produce crystalline, ionic compounds such as $(S_8)(AsF_6)_2$,¹ $(Se_{10})(SbF_6)_2$,² and $(Te_6)(AsF_6)_4(SO_2)_2$.³ Mixtures of chalcogens have been oxidized to give salts containing mixtures of homopolyatomic cations such as $(Te_6)(Se_8)(AsF_6)_6(SO_2)_4$ or heteropolyatomic cations such as $(Te_3S_3)(AsF_6)_2$,⁵ $(Te_2Se_2)(Sb_3F_{14})(SbF_6)_6$,⁶ and $(Te_2Se_8)(AsF_6)_2(SO_2)$.⁷ In the present work we carried out reactions with stoichiometries that might have led to cations such as $Te_2Se_{10}^{2+}$, $Te_2Se_{14}^{2+}$, and $Te_2S_2Se_2^{2+}$, but instead we obtained new salts of the $Te_2Se_8^{2+}$ cation and a salt containing

the new $Te_2Se_6^{2+}$ cation. Although the $Te_2Se_8^{2+}$ cation is isostructural with the Se_{10}^{2+} cation,^{2,8} the $Te_2Se_6^{2+}$ cation is not isostructural with the Se_8^{2+} cation^{4,9} but has a novel cubelike structure unlike that of any of the previously known polyatomic cations of the chalcogens.

Experimental Section

Materials. Elemental sulfur (BDH), selenium (Koch-Light Laboratories Ltd., 99.95%), and tellurium (Koch-Light Laboratories Ltd., 99.7%) were dried under vacuum at room temperature overnight before use. Antimony pentafluoride (Ozark-Mahoning) was distilled under vacuum and stored in an FEP bottle. Arsenic pentafluoride was prepared from the elements in a nickel can on a Monel vacuum line and stored in a nickel cylinder. Sulfur dioxide (Canadian Liquid Air) was stored over P_4O_{10} for at least 24 h before use. All reactions were carried out under vacuum in flame-sealed, double-bulb vessels fitted with medium porosity glass frits. Solid transfers were done in nitrogen-filled dryboxes.

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Table I. Unit Cell Dimensions and Crystal Data for the Decaatomic Tellurium-Selenium Cations

	(Te ₂ Se ₈)(AsF ₆) ₂ SO ₂ ^a	(Te ₂ Se ₆)(Te ₂ Se ₈)- (AsF ₆) ₄ (SO ₂) ₂	(Te ₂ Se ₈)(AsF ₆) ₂	(Te ₂ Se ₈)(SbF ₆) ₂	(Te _x Se _y)(AsF ₆) ₂	
syst	monoclinic	monoclinic	orthorhombic	orthorhombic	orthorhombic	
<i>a</i> , Å	7.337 (2)	12.432 (4)	16.118 (3)	16.489 (3)	14.790 (3)	14.840 (6) ^a
<i>b</i> , Å	8.545 (3)	15.956 (6)	13.098 (3)	13.251 (4)	10.783 (2)	10.828 (5)
<i>c</i> , Å	36.030 (2)	23.053 (10)	18.951 (4)	19.422 (6)	13.304 (2)	13.345 (5)
β, deg	91.52 (5)	96.61 (3)				
<i>V</i> , Å ³	2258.4	4542 (3)	4000.6 (13)	4244 (2)	2121.7 (7)	2144
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>Pbcn</i>	<i>Pbcn</i>	<i>Pbcn</i>	<i>Pbcn</i>
<i>Z</i>	4	4	8	8	4	4
<i>D</i> _{calcd} , g cm ⁻³	3.90	3.66	4.20	4.25	~4.22	4.16
μ, cm ⁻¹	198	180	222.4		202	
reflens used in cell determ	15 (15 < 2θ < 25°)	14 (24 < 2θ < 28°)	15 (26 < 2θ < 30°)	15 (26 < 2θ < 29°)	15 (28 < 2θ < 32°)	

^a Reference 7.Table II. Details of Data Collections and Structure Refinements^a

compd	(Te ₂ Se ₆)(Te ₂ Se ₈)(AsF ₆) ₄ (SO ₂) ₂ ^b	(Te ₂ Se ₈)(AsF ₆) ₂ ^b	(Te _x Se _y)(AsF ₆) ₂
max 2θ, deg; scan type	45; θ-2θ	55; θ-2θ	55; θ-2θ
scan range, deg	(Kα ₁ - 1.0) to (Kα ₂ + 1.0)	(Kα ₁ - 0.90°) to (Kα ₂ + 0.90°)	(Kα ₁ - 0.95°) to (Kα ₂ + 0.95°)
scan rates, deg/min ^c	3.0-29.3	3.0-29.3	2.0-29.3
std reflcns, no./interval ^d	3/67	3/67	3/67
quadrants collected	<i>h, k, ±l</i>	<i>h, k, l</i>	<i>h, k, l</i>
no. of data collected (including stds) ^e	7024	5833	3523
abs cors ^f (faces used; dist from origin within cryst, mm)	ABSORB ^g ({0,0,1}, 0.025; {1,0,0}, 0.120; {0,1,0}, 0.075)	ABSORB ^g ({1,0,0}, 0.051; {0,0,1}, 0.058; {0,1,0}, 0.390; ($\bar{1}$,1,1), 0.035)	ABSORB ^g ({1,1,0}, 0.043; {0,0,1}, 0.460)
grid	7 × 7 × 12	10 × 7 × 10	10 × 10 × 6
<i>A</i> ^h	2.43-13.83	5.81-12.82	3.61-7.30
no. of non-zero data	4826	3866	2179
no. of data <i>F</i> > 6σ(<i>F</i>)	2290	2130	1555
structure soln ^h	direct methods (SHELX)	direct methods (SHELX)	use of some positions from ref 7
<i>R</i> factors			
6σ(<i>F</i>): <i>R</i> ₁ (<i>R</i> ₂)	0.0754 (0.0773)	0.0473 (0.0455)	0.0304 (0.0313)
all: <i>R</i> ₁ (<i>R</i> ₂)	0.1607 (0.1759)	0.1252 (0.0967)	0.0542 (0.0430)
max shift/error, %	9	34	14
<i>G</i> of weighting scheme, w ⁻¹ = σ(<i>F</i>) ² + <i>GF</i> ²	0.00179	0.00070	0.00037
final diff Fourier max peak, e/Å ³	1.5 (0.76, 0.02, 0.51)	2.0 (near Te(2))	1.0 (near F(4)), 0.8 (near Te(2))

^aSyntex P2, diffractometer, graphite-monochromatized Mo Kα radiation (λ = 0.71069 Å). Stationary background counts recorded at each end of the scan, each for one-fourth of the scan time. ^bSee text for discussions on compositions of these two compounds. ^cDependent on intensity of prescan. ^dDuring each data collection the standard reflections showed only statistical fluctuations in intensities. ^eLorentz and polarization corrections applied to all data collected. ^fApplied toward the end of each refinement when the compositions of the compounds were known. Symmetry-equivalent reflections were averaged and those with *F*_{obsd} = 0.0 then excluded to give the final numbers of independent data indicated. ^gPrograms: XRAY 76¹⁰ and SHELX¹⁰ on CDC computers. ^h*F* and Δ*F* Fourier maps for missing atoms.

Preparation of (Te₂Se₈)(AsF₆)₂ (1a). Arsenic pentafluoride (0.243 g, 1.43 mmol) was distilled onto a mixture of Te (0.1148 g, 0.900 mmol) and Se (0.5002 g, 6.33 mmol) powders and 25 mL of SO₂ in one bulb of a double-bulb vessel cooled to -196 °C. When the system was warmed, the solvent melted to give a green solution that turned brown after 1 h. The mixture was stirred for 4 days, filtered through a glass frit into the other bulb of the vessel, and allowed to stand for 1 week. A large quantity of shiny, black needles formed from the solution and were identified as (Te₂Se₈)(AsF₆)₂ by X-ray crystallography.

Preparation of (Te₂Se₈)(SbF₆)₂ (1b). Antimony pentafluoride (1.668 g, 7.70 mmol) was transferred into one bulb of a double-bulb vessel, and 40 mL of SO₂ was condensed onto the SbF₅. This solution was poured into the other bulb of the vessel containing a mixture of Te (0.6572 g, 5.15 mmol) and Se (2.0256 g, 25.65 mmol) powders. The initial green solution turned brown during the first 1 h of stirring. After the mixture was heated at 60 °C for 12 h, most of the product had precipitated, leaving a pale green solution, which returned to a deep brown color upon stirring for a further 24 h at 22 °C. The solution was filtered, and a large number of shiny, black needles were formed from the filtrate. Precession photographs revealed that the crystals were isomorphous with 1a.

Preparation of (Te_{4.5}Se_{5.5})(AsF₆)₂ (2). By the above procedure, AsF₅ (0.607 g, 3.58 mmol) was combined with Te (0.7786 g, 6.10 mmol) and Se (0.4804 g, 6.08 mmol) in 40 mL of SO₂. After 24 h of stirring a large quantity of a dark brown powder had precipitated. Since the solubility of many salts of the group 16 polyatomic cations in SO₂ increases with decreasing temperature, the reaction mixture was cooled to just above the freezing point of the solution before filtering. The filtrate was allowed to slowly warm to room temperature over a period of 48 h. The resulting brown-black crystals and powder were isolated and identified as (Te_{4.5}Se_{5.5})(AsF₆)₂ by X-ray crystallography.

Preparation of (Te₂Se₆)(Te₂Se₈)(AsF₆)₄(SO₂)₂ (3). Sulfur dioxide (30 mL) and AsF₅ (2.33 g, 13.7 mmol) were condensed onto a mixture of powdered Te (1.82 g, 14.3 mmol), Se (1.13 g, 14.3 mmol), and S (0.458 g, 14.3 mmol). The initial green solution turned red within 5 min of stirring. After 1 h a large quantity of a brown powder had precipitated from the red-brown solution. No further change was observed after 8 h, and the solution was filtered. When no crystals were obtained after 48 h, the solvent was slowly distilled off over 2 weeks to give a large quantity of dark brown crystals. These were isolated under somewhat less than 1 atm of SO₂ by pouring the solution into the other half of the vessel and cooling to -30 °C before flame-sealing the bulb containing the crystals. X-ray crystallography identified the compound as (Te₂Se₆)(Te₂Se₈)(AsF₆)₄(SO₂)₂.

X-ray Crystallography. All crystals were selected and sealed in dry Lindemann capillaries in a drybox equipped with a microscope. Precession photographs were used to check crystal quality and to obtain preliminary cell and symmetry information. Crystals of (Te₂Se₆)(Te₂Se₈)(AsF₆)₄(SO₂)₂ lose SO₂ from the lattice over time, and so the crystal quality of this compound was not as good as that for 1a, 1b, or 2. Further work on the diffractometer at 298 K gave the crystal data summarized in Table I. Intensity data on each compound were collected by using the options specified in Table II. Data treatment and structure solutions were as indicated. Least-squares refinements minimizing ΣwΔ*F*² converged to the residuals in Table II. Final atomic positional parameters are given in Table III. Scattering curves were taken from ref 11 or were

(11) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV (present distributor D. Reidel, Dordrecht, The Netherlands).

Table III. Final Atomic Positional Parameters ($\times 10^4$)

atom	x	y	z	atom	x	y	z
(a) $(\text{Te}_2\text{Se}_8)(\text{AsF}_6)_2$ (1a)							
Te(1)	2462.6 (8)	2197.4 (9)	5335.2 (5)	F(11)	4735 (8)	1700 (9)	1575 (8)
Te(2)	3612.4 (8)	2814.5 (9)	2987.3 (6)	F(12)	3631 (9)	-432 (10)	1146 (7)
Se(1)	3552 (1)	1187 (1)	4639 (1)	F(13)	4986 (10)	64 (11)	1118 (15)
Se(2)	2986 (1)	1189 (1)	3528 (1)	F(14)	4131 (17)	275 (20)	2170 (8)
Se(3)	2218 (1)	3657 (1)	2646 (1)	F(15)	3986 (19)	1149 (13)	592 (10)
Se(4)	1207 (1)	2484 (1)	2910 (1)	F(16)	3305 (11)	1266 (20)	1639 (18)
Se(5)	737 (1)	2959 (1)	4037 (1)	F(21)	5536 (6)	5301 (8)	4376 (5)
Se(6)	1121 (1)	1595 (1)	4721 (1)	F(22)	5500 (8)	4071 (8)	3417 (7)
Se(7)	2628 (1)	3866 (1)	4630 (1)	F(23)	6803 (7)	4600 (9)	3884 (6)
Se(8)	3927 (1)	3716 (1)	4158 (1)	F(24)	6397 (7)	5097 (8)	2699 (5)
As(1)	4177 (1)	633 (1)	1358 (1)	F(25)	6437 (7)	6372 (8)	3669 (6)
As(2)	5962 (1)	5226 (1)	3538 (1)	F(26)	5135 (7)	5820 (9)	3199 (5)
(b) $(\text{Te}_{4.5}\text{Se}_{5.3})(\text{AsF}_6)_2$ (2)							
Te(1)	1678.4 (3)	3944.9 (5)	2304.6 (4)	F(1)	658 (3)	1414 (7)	-147 (4)
Te(2)	683.7 (5)	2707.0 (7)	3654.2 (5)	F(2)	1435 (5)	1011 (8)	1400 (5)
Se(1)	377.3 (6)	4363.9 (9)	1032.9 (6)	F(3)	1306 (6)	-573 (6)	178 (7)
Se(2)	4260.4 (5)	2386.2 (7)	2040.8 (6)	F(4)	2109 (5)	2313 (7)	212 (8)
Se(3)	3343.9 (5)	1124.0 (8)	3164.4 (6)	F(5)	2750 (4)	334 (6)	484 (4)
As	1690.6 (6)	859.7 (9)	176.8 (7)	F(6)	1996 (4)	795 (8)	-1027 (4)
(c) $(\text{Te}_2\text{Se}_6)(\text{Te}_2\text{Se}_8)(\text{AsF}_6)_4(\text{SO}_2)_2$ (3)							
Te(1)	5153 (3)	1755 (2)	2983 (2)	F(15)	410 (5)	240 (4)	119 (3)
Te(2)	4362 (3)	3929 (2)	4324 (2)	F(16)	371 (5)	120 (4)	63 (3)
Te(3)	-154 (3)	847 (2)	1964 (2)	F(21)	1003 (4)	68 (3)	-129 (2)
Te(4)	-298 (3)	3429 (2)	1232 (2)	F(22)	1084 (6)	210 (4)	-123 (3)
Se(3)	6633 (6)	2726 (4)	2725 (3)	F(23)	1005 (4)	143 (3)	-40 (3)
Se(4)	7769 (5)	2898 (4)	3584 (3)	F(24)	1192 (4)	80 (3)	-118 (2)
Se(5)	7237 (5)	4235 (4)	3904 (3)	F(25)	1118 (5)	23 (4)	-50 (3)
Se(6)	6382 (5)	3899 (4)	4699 (3)	F(26)	1196 (4)	161 (3)	-29 (2)
Se(7)	3912 (4)	2348 (3)	4345 (3)	F(31)	-281 (4)	80 (3)	362 (2)
Se(8)	5525 (5)	1797 (3)	4108 (3)	F(32)	-277 (4)	54 (3)	254 (2)
Se(9)	3609 (4)	2836 (3)	2877 (3)	F(33)	-179 (4)	-67 (3)	272 (2)
Se(10)	4525 (4)	4043 (3)	3212 (3)	F(34)	-179 (5)	-45 (4)	379 (3)
Se(11)	-671 (5)	3127 (3)	2285 (3)	F(35)	-104 (6)	43 (4)	322 (3)
Se(12)	560 (5)	2123 (3)	2584 (3)	F(36)	-346 (8)	-46 (5)	308 (4)
Se(13)	-1992 (4)	1537 (4)	1557 (3)	F(41)	730 (3)	607 (2)	229 (2)
Se(14)	-1537 (5)	2243 (4)	753 (3)	F(42)	745 (3)	415 (2)	169 (2)
Se(15)	1510 (4)	2555 (3)	1282 (3)	F(43)	862 (3)	531 (2)	181 (2)
Se(16)	796 (4)	1205 (3)	1043 (3)	F(44)	680 (3)	555 (2)	136 (2)
As(1)	4605 (5)	1566 (3)	1171 (3)	F(45)	792 (3)	469 (2)	263 (2)
As(2)	10995 (5)	1150 (3)	-796 (3)	F(46)	612 (3)	487 (2)	220 (2)
As(3)	-2240 (5)	64 (3)	3177 (3)	S(1) ^a	505 (0)	409 (0)	72 (0)
As(4)	7361 (4)	5105 (3)	1989 (3)	S(2) ^a	48 (0)	118 (0)	448 (0)
F(11)	385 (5)	118 (4)	160 (3)	O(11) ^a	398 (0)	427 (0)	47 (0)
F(12)	542 (4)	188 (3)	69 (2)	O(12) ^a	597 (0)	387 (0)	44 (0)
F(13)	522 (5)	67 (3)	115 (3)	O(21) ^a	-60 (0)	136 (0)	455 (0)
F(14)	557 (5)	180 (4)	164 (3)	O(22) ^a	145 (0)	80 (0)	473 (0)

^a Atoms were located in a ΔF Fourier and constrained in least squares to have S-O bond lengths of 1.40 ± 0.04 Å before their positional parameters were fixed in final cycles of least squares.

stored in the programs.

Discussion

In the preparation of $(\text{Te}_2\text{Se}_8)(\text{AsF}_6)_2$ and $(\text{Te}_2\text{Se}_8)(\text{SbF}_6)_2$ the reagent stoichiometries were such that they could, in principle, have produced cations of average oxidation state $< +0.2$, that is $\text{Te}_2\text{Se}_{14}^{2+}$ and $\text{Te}_2\text{Se}_{10}^{2+}$ respectively. In both cases, however, the resulting crystalline compounds contained only the $\text{Te}_2\text{Se}_8^{2+}$ cation (Figure 1). In an earlier study² we were unable to prepare salts of selenium polyatomic cations containing the element in a lower formal oxidation state than in Se_{10}^{2+} , although there is some potentiometric and spectrophotometric evidence for the presence of Se_{16}^{2+} and Se_{12}^{2+} cations in NaCl-AlCl_3 melts.¹² The Se_{19}^{2+} cation remains the only chalcogen polyatomic cation with an average oxidation state $< +0.2$ that has been characterized by X-ray crystallography.¹³

The $\text{Te}_x\text{Se}_{10-x}^{2+}$ Cation. Bond lengths of the $\text{Te}_x\text{Se}_{10-x}^{2+}$ cation in 1a, 2, and 3 are compared with those for the cation in $(\text{Te}_2-$

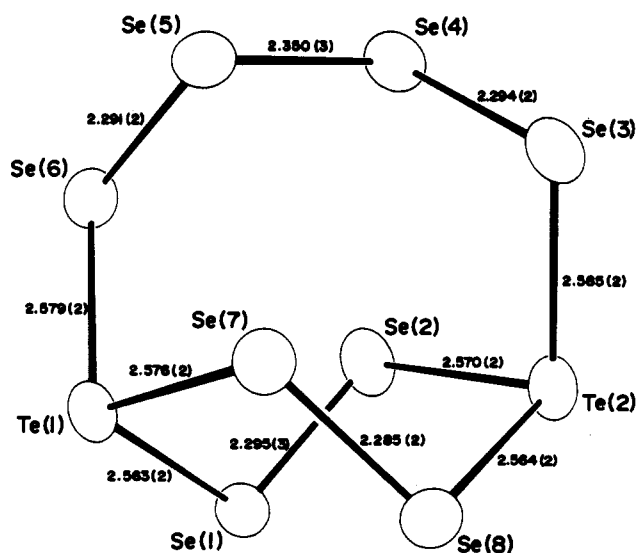


Figure 1. The $\text{Te}_2\text{Se}_8^{2+}$ cation in $(\text{Te}_2\text{Se}_8)(\text{AsF}_6)_2$.

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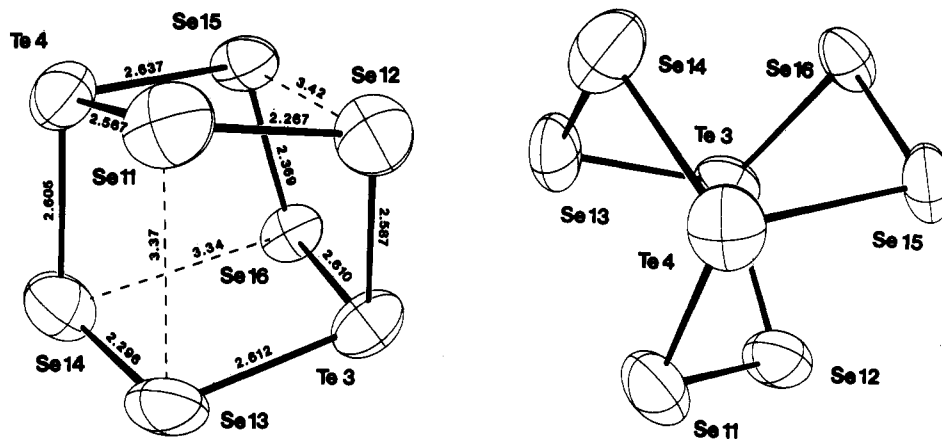


Figure 2. The $\text{Te}_2\text{Se}_6^{2+}$ cation in $(\text{Te}_2\text{Se}_6)(\text{Te}_2\text{Se}_8)(\text{AsF}_6)_4(\text{SO}_2)_2$. Esd's on bond lengths are 0.006–0.010 Å. Bond angles (deg) are as follows: $\text{Se}(12)\text{--Te}(3)\text{--Se}(13) = 95.6$ (2); $\text{Se}(12)\text{--Te}(3)\text{--Se}(16) = 96.8$ (2); $\text{Se}(13)\text{--Te}(3)\text{--Se}(16) = 94.3$ (2); $\text{Se}(11)\text{--Te}(4)\text{--Se}(14) = 95.9$ (2); $\text{Se}(11)\text{--Te}(4)\text{--Se}(15) = 96.0$ (2); $\text{Se}(14)\text{--Te}(4)\text{--Se}(15) = 95.4$ (2); $\text{Te}(4)\text{--Se}(11)\text{--Se}(12) = 103.3$ (3); $\text{Te}(3)\text{--Se}(12)\text{--Se}(11) = 102.2$ (3); $\text{Te}(4)\text{--Se}(15)\text{--Se}(16) = 100.2$ (2); $\text{Te}(3)\text{--Se}(16)\text{--Se}(15) = 101.6$ (3).

Table IV. Bond Lengths and Bond Angles in the $\text{Te}_x\text{Se}_{10-x}^{2+}$ Cation

	$(\text{Te}_2\text{Se}_8)(\text{AsF}_6)_2^a$	$(\text{Te}_2\text{Se}_8)(\text{AsF}_6)_2\text{SO}_2^b$	$(\text{Te}_2\text{Se}_6)(\text{Te}_2\text{Se}_8)(\text{AsF}_6)_4(\text{SO}_2)_2^a$	$(\text{Te}_x\text{Se}_y)(\text{AsF}_6)_2^{a,b}$	
Bond Distances (Å)					
Te(1)–Se(1)	2.563 (2)	2.643 (8)	2.572 (6)	2.602 (1)	2.61 (1)
Te(1)–Se(6)	2.579 (2)	2.579 (8)	2.529 (8)	2.614 (1)	2.63 (1)
Te(1)–Se(7)	2.576 (2)	2.644 (8)	2.582 (8)	2.678 (1) ^c	2.66 (5)
Te(2)–Se(2)	2.570 (2)	2.613 (8)	2.600 (7)	2.678 (1) ^c	2.73 (3)
Te(2)–Se(3)	2.585 (2)	2.602 (8)	2.560 (7)	2.614 (1)	2.63 (1)
Te(2)–Se(8)	2.564 (2)	2.583 (8)	2.586 (6)	2.602 (1)	2.61 (1)
Se(1)–Se(2)	2.295 (3)	2.373 (8)	2.324 (7)	2.414 (1)	2.53 (4)
Se(3)–Se(4)	2.294 (2)	2.328 (8)	2.284 (10)	2.434 (1)	2.50 (2)
Se(4)–Se(5)	2.350 (3)	2.401 (8)	2.375 (9)	2.506 (2)	2.54 ^d
Se(5)–Se(6)	2.291 (2)	2.318 (8)	2.314 (10)	2.434 (1)	2.43 ^d
Se(7)–Se(8)	2.285 (2)	2.356 (8)	2.312 (8)	2.414 (1)	2.31 (5)
Bond Angles (deg)					
Se(1)–Te(1)–Se(6)	100.64 (6)	97.6 (2)	97.0 (2)	96.84 (3)	97 (1)
Se(1)–Te(1)–Se(7)	95.76 (6)	96.1 (2)	97.1 (2)	96.68 (3)	99 (1)
Se(6)–Te(1)–Se(7)	96.41 (6)	97.8 (2)	99.8 (2)	98.51 (3)	99 (1)
Se(2)–Te(2)–Se(3)	96.42 (6)	97.6 (2)	100.5 (2)	98.51 (3)	97 (1)
Se(2)–Te(2)–Se(8)	96.54 (7)	97.1 (2)	97.3 (2)	96.68 (3)	94 (1)
Se(3)–Te(2)–Se(8)	101.04 (7)	98.2 (2)	98.6 (2)	96.84 (3)	97 (1)
Te(1)–Se(1)–Se(2)	101.50 (7)	97.5 (2)	101.1 (2)	103.89 (4)	102 (1)
Te(2)–Se(2)–Se(1)	102.18 (7)	99.9 (2)	100.3 (3)	95.95 (4)	100 (-)
Te(2)–Se(3)–Se(4)	106.11 (7)	100.5 (2)	104.7 (3)	103.96 (4)	103 (1)
Se(3)–Se(4)–Se(5)	104.42 (8)	101.5 (2)	102.1 (3)	100.78 (4)	102 (-)
Se(4)–Se(5)–Se(6)	102.76 (8)	104.2 (2)	102.0 (3)	100.78 (4)	99 (-)
Se(5)–Se(6)–Te(1)	104.12 (7)	104.9 (2)	105.0 (3)	103.96 (4)	104 (1)
Te(1)–Se(7)–Se(8)	102.98 (7)	102.1 (2)	100.7 (3)	103.89 (4)	93 (-)
Se(7)–Se(8)–Te(2)	101.36 (8)	102.8 (2)	99.9 (3)	95.95 (4)	105 (1)

^aThis work. ^bReference 7. ^cAtomic numbering corresponds to $(\text{Te}_2\text{Se}_8)(\text{AsF}_6)_2$ (Figure 1). $\text{Se}(7) \equiv \text{Te}(2)$ in the $\text{Te}_x\text{Se}_y^{2+}$ cation, which has crystallography symmetry 2 such that "Se1" = "Se8", "Se2" = "Se7", and "Se4" = "Se5". ^dStandard error uncertain.

Table V. Occupation of the Sites in the $\text{Te}_x\text{Se}_{10-x}^{2+}$ Cation^a

atomic site	population parameter	no. of electrons	% Te	% Se
Te(1)	0.998 (4)	51.9 (2)	100 (1)	0 (1)
Te(2)	0.844 (3)	43.9 (2)	55 (1)	45 (1)
Se(1)	1.064 (4)	36.2 (2)	12 (1)	88 (1)
Se(2)	1.230 (5)	41.8 (2)	43 (1)	57 (1)
Se(3)	1.068 (5)	36.3 (2)	13 (1)	87 (1)

^aOverall composition: $\text{Te}_{4.46(5)}\text{Se}_{5.54(5)}^{2+}$.

$\text{Se}_8)(\text{AsF}_6)_2(\text{SO}_2)$ and $(\text{Te}_{3.7}\text{Se}_{6.3})(\text{AsF}_6)_2$ in Table IV. The cation in **2** is a disordered mixture of $\text{Te}_x\text{Se}_{10-x}^{2+}$ cations (cf. ref 7) and has the overall composition $\text{Te}_{4.5}\text{Se}_{5.5}^{2+}$ based on the refined population parameters of the Te and Se sites (Table V). Bond lengths in $\text{Te}_{4.5}\text{Se}_{5.5}^{2+}$ are significantly longer than those of the $\text{Te}_2\text{Se}_8^{2+}$ cation in **1a** or **3**, as would be expected for partial substitution of Te at the Se sites of $\text{Te}_2\text{Se}_8^{2+}$, but they are, on average, less than those of the cations in $(\text{Te}_{3.7}\text{Se}_{6.3})(\text{AsF}_6)_2^7$ and $(\text{Te}_2\text{Se}_8)(\text{AsF}_6)_2(\text{SO}_2)^7$ (Table IV). This is surprising and

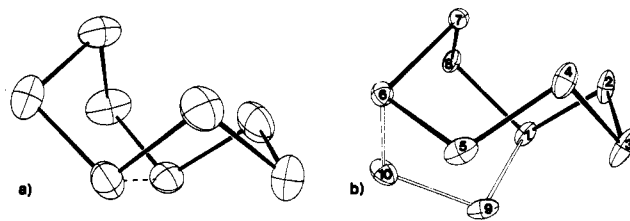


Figure 3. The Se_8^{2+} cation (a) and the Se_{10}^{2+} cation (b) showing the Se_8^{2+} structure (filled-in bonds) within the Se_{10}^{2+} structure (redrawn from coordinates in ref 4 and 8, respectively).

probably indicates that the cations in $(\text{Te}_2\text{Se}_8)(\text{AsF}_6)_2(\text{SO}_2)$ and $(\text{Te}_{3.7}\text{Se}_{6.3})(\text{AsF}_6)_2$ contain more tellurium and less selenium than was realized when these structures were determined. In $(\text{Te}_2\text{Se}_8)(\text{AsF}_6)_2$, the central bond in the four-atom Se chain, $\text{Se}(4)\text{--Se}(5)$, is somewhat longer than the other Se–Se bond lengths, but this is probably not due to any substitution of tellurium in these positions, because a similar lengthening of this bond has been

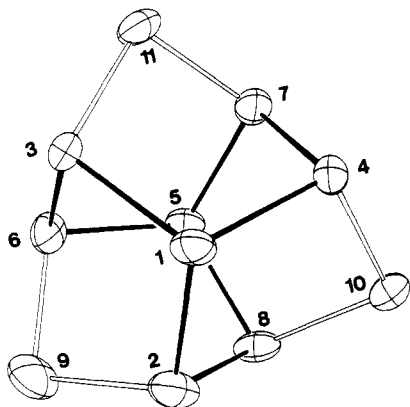


Figure 4. The As_{11}^{3-} anion, redrawn from coordinates in ref 19. Filled-in bonds indicate the $\text{Te}_2\text{Se}_6^{2+}$ -like core (cf. Figure 2).

observed in Se_{10}^{2+} and in chains of four or more sulfur atoms.^{2,8,14}

The $\text{Te}_2\text{Se}_6^{2+}$ Cation. The structure of the $\text{Te}_2\text{Se}_6^{2+}$ cation is very different from that of Se_8^{2+} (Figures 2 and 3). The S_8^{2+} and Se_8^{2+} cations are eight-membered rings with an exo-endo conformation and a long transannular bond giving an approximately bicyclo[3.3.0]octane geometry.^{1,4,9} This arrangement has been described¹⁵ as being halfway between the crown-shaped ring of S_8 (or S_8) and the S_4N_4 structure, which is isoelectronic with the unknown S_8^{4+} cation. The $\text{Te}_2\text{Se}_6^{2+}$ cation, however, has a bicyclo[2.2.2]octane structure with the two tellurium atoms occupying the bridgehead positions (Figure 2). This structure approximates to a distorted cube with three edges (the nonbonded edges in the valence-bond description) that are considerably longer than the other nine.

The Te-Se bonds in $\text{Te}_2\text{Se}_6^{2+}$ have lengths of 2.567 (9)–2.637 (6) Å, and the average of 2.603 Å is significantly longer than the sum of the covalent radii (2.54 Å) and the average Te-Se distance of 2.57 Å in $(\text{Te}_2\text{Se}_6)(\text{AsF}_6)_2$ and the $\text{Te}_2\text{Se}_8^{2+}$ cation in $(\text{Te}_2\text{Se}_6)(\text{Te}_2\text{Se}_8)(\text{AsF}_6)_4(\text{SO}_2)_2$. Moreover, the Se(15)–Se(16) bond is significantly longer than the other two Se–Se bonds (Figure 2), and the Te(4)–Se(15) bond is longer than the average of the Te–Se bonds. These bond lengths suggest that the Se(15) site may be partially occupied by tellurium.¹⁶ The average Se–Te–Se angle of 95.6° in $\text{Te}_2\text{Se}_6^{2+}$ is significantly smaller than the analogous angles of 99.72 and 98.35° in the $\text{Te}_2\text{Se}_8^{2+}$ cation in **1a** and **3**, respectively.

An interesting feature in the $\text{Te}_2\text{Se}_6^{2+}$ cation are the three short transannular Se...Se contacts of lengths 3.34, 3.37, and 3.42 Å, that is, ca. 0.46–0.38 Å shorter than van der Waals distances. Contacts of similar length (3.30–3.49 Å) in the Se_{10}^{2+} cation^{2,8} have been considered to be weak "bonds". They correspond to three bonds of the parent cuneane structure, each of which have been broken by the addition of an electron pair.¹⁵ Similarly the short Se...Se contacts in $\text{Te}_2\text{Se}_6^{2+}$ can be considered to result from the breaking of three edges of a cube by the addition of three electron pairs. Many of the main-group cages can be derived from a few basic cluster geometries in this fashion.^{15,17} That these Se...Se contacts in $\text{Te}_2\text{Se}_6^{2+}$ represent weak cross-ring bonding is supported by the structures of the P_{11}^{3-} and As_{11}^{3-} anions.^{18,19} In P_{11}^{3-} and As_{11}^{3-} three edges of a cube are broken by the addition

of bridging atoms rather than electron pairs.¹⁵ The resulting structures are remarkably similar (compare Figures 2 and 4).

In another view of the structure of $\text{Te}_2\text{Se}_6^{2+}$ it can be considered to be derived from an idealized bicapped-trigonal-prism (D_{3h}) geometry. However, in this structure all the lone pairs on selenium are eclipsed. But these lone pair repulsions can be reduced by increasing the Te–Se–Se–Te dihedral angle. A similar situation exists for cyclohexane, where the twist-boat conformation, with all C–H bonds staggered, is 1.6 kcal lower in energy than the boat, where the C–H bonds are eclipsed along two of the C–C bonds.²⁰ The $\text{Te}_2\text{Se}_6^{2+}$ cation can be viewed as consisting of three fused twist boats. A perfect tetrahedral geometry about each selenium atom and a dihedral angle of 60° would result in staggered lone pairs on adjacent selenium atoms. Since lone pairs generally exert a greater repulsive effect than bond pairs,²¹ the projected lone-pair–lone-pair angle would be expected to be greater than 120° and the most favorable dihedral angle then somewhat greater than 60°. The Te–Se–Se–Te dihedral angles in the $\text{Te}_2\text{Se}_6^{2+}$ cation of 68.9, 69.2, and 69.3° are very close to that expected for the most favorable lone-pair geometry.

The $\text{Te}_2\text{Se}_6^{2+}$ and Se_8^{2+} structures can also be related to each other by considering the structures of $\text{Te}_2\text{Se}_8^{2+}$ and Se_{10}^{2+} . Figure 3b demonstrates that removal of atoms Se(9) and Se(10) in Se_{10}^{2+} and the formation of a long transannular bond between Se(1) and Se(5) result in the exo-endo eight-membered ring of Se_8^{2+} . Formation of $\text{Te}_2\text{Se}_6^{2+}$ from $\text{Te}_2\text{Se}_8^{2+}$ in a fashion similar to that for Se_8^{2+} from Se_{10}^{2+} would, however, result in atoms Te(2) and Se(6) forming the transannular bond and Te(1) becoming only two-coordinate (Figure 1). Since tellurium is more electropositive than selenium, a more favorable structure would have both tellurium atoms in the three-coordinate positions, where the positive charge is presumably mainly located (cf. $\text{Te}_2\text{Se}_8^{2+}$ and $\text{Te}_2\text{Se}_4^{2+}$).^{5,22} Formation of $\text{Te}_2\text{Se}_6^{2+}$ by removal of two atoms from the four-atom selenium chain, however, allows both tellurium atoms to remain three-coordinate, and the resulting cubelike structure is favored over the Se_8^{2+} -like structure.

The $\text{Te}_2\text{Se}_4^{2+}$, $\text{Te}_2\text{Se}_6^{2+}$, and $\text{Te}_2\text{Se}_8^{2+}$ structures can be readily interpreted by using electron-precise, localized bond descriptions whereas many homopolyatomic cations and anions adopt structures that allow for charge delocalization. Thus, the trigonal-prismatic Te_6^{4+} and square-planar S_4^{2+} , Se_4^{2+} , and Te_4^{2+} cations^{3,23} exhibit complete charge delocalization with all atoms equivalent, the P_6^{4-} anion is a regular hexagon,²⁴ and the same structure has been proposed for the isoivalent Te_6^{2+} cation.²⁵ The charge-delocalized structure of Te_6^{2+} is presumed to be more stable than a structure with localized bonding as observed in the related $\text{Te}_2\text{Se}_4^{2+}$ cation. Molecular orbital calculations have revealed that there is considerable delocalization of charge in the S_8^{2+} and Se_8^{2+} structures and that the observed structure is the most stable for these cations.^{25,26} The large electronegativity difference between tellurium and selenium, however, is apparently of greater importance in determining the structures of the mixed Te–Se cations. Since the electronegativity difference between selenium and sulfur is small, the hypothetical mixed $\text{S}_x\text{Se}_{8-x}^{2+}$ cations would be expected to adopt the Se_8^{2+} structure, while $\text{Te}_2\text{S}_6^{2+}$ should be isostructural with $\text{Te}_2\text{Se}_6^{2+}$.

One might have expected the Se_{10}^{2+} cation to adopt a charge-delocalized structure, yet Se_{10}^{2+} has the same solid-state structure as $\text{Te}_2\text{Se}_8^{2+}$. Spectroscopic evidence suggests, however,

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(16) Unfortunately the data set was not good enough to give realistic values for the population parameters (PP) of the Te and Se atoms in an unconstrained least-squares refinement (the range of values 0.92 (2)–1.16 (2) was obtained but with consistently high values of PP's ~1.1 for the Te atoms, presumably due to the low contribution to the structure factors from the lighter atoms).

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that Se_{10}^{2+} may not retain this structure in solution. There is a considerable difference between the solution and solid-state electronic spectra of the Se_{10}^{2+} cation,² and ^{77}Se NMR studies have provided evidence for intramolecular exchange and isomerization in both SO_2 and 100% H_2SO_4 solution.²⁷ In contrast, the ^{77}Se NMR spectrum of $\text{Te}_2\text{Se}_8^{2+}$ in 100% H_2SO_4 shows no sign of exchange and is consistent with the solid-state structure.²⁸ The $\text{Te}_2\text{Se}_6^{2+}$ and Se_8^{2+} cations also retain their unique solid-state structures in solution.^{27,29}

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Registry No. **1a**, 58249-21-1; **1b**, 107453-36-1; **2**, 107556-03-6; 3, 107453-35-0; **Te**, 13494-80-9; **Se**, 7782-49-2; **AsF₃**, 7784-36-3; **SO₂**, 7446-09-5; **SbF₅**, 7783-70-2; **S**, 7704-34-9.

Supplementary Material Available: Tables VI and VII, containing bond distances and bond angles in the anions and final anisotropic thermal parameters, respectively (7 pages); Table VIII, containing final structure factor amplitudes (43 pages). Ordering information is given on any current masthead page.

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Crystal Structure and Magnetic and EPR Studies of Bis[cinchoninium tetrachlorocuprate(II)] Trihydrate Single Crystals with a Weak Exchange Coupling

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The crystal structure of bis[cinchoninium tetrachlorocuprate(II)] trihydrate, $[(\text{C}_{19}\text{H}_{24}\text{N}_2\text{O})\text{CuCl}_4]_2 \cdot 3\text{H}_2\text{O}$, has been established by single-crystal X-ray diffraction methods. The crystals are orthorhombic, space group $P2_12_12_1$, with unit cell parameters $a = 15.414$ (3), $b = 36.719$ (6), and $c = 7.974$ (2) Å for $Z = 4$. The asymmetric unit consists of two tetrahedral CuCl_4^{2-} anions, which are linked to two doubly protonated cinchonine molecules and three water molecules by hydrogen bonds. The CuCl_4^{2-} tetrahedrons are approximately D_{2d} flattened with the average Cl-Cu-Cl angle along the flattening axes being 145° and the (Cu-Cl) distance being 2.25 Å. The magnetic susceptibility obeys the Curie law in the temperature range from 4.2 to 350 K, and the crystal can be treated as magnetically diluted. The exchange coupling between magnetically nonequivalent Cu(II) ions, determined from a computer analysis of two-component EPR spectra, is $|J| = 0.0030$ (5) cm^{-1} at 298 K and increases at low temperatures. Reflectance UV-vis spectra contain d-d bands, $xy \rightarrow (xz,yz) = 9100$ cm^{-1} and $xy \rightarrow z^2 = 11\,100$ cm^{-1} , and charge-transfer bands at 22 500 and 26 000 cm^{-1} . The band positions are analyzed in terms of ligand field theory, by addition to the crystal field electrostatic terms of the destabilization terms from covalency of the Cu-Cl bonds described by the angular overlap model. The EPR parameters, $g_{\parallel} = 2.292$ (4) and $g_{\perp} = 2.051$ (4), are discussed in terms of the MO theory, including charge-transfer, orbital overlap, and ligand spin-orbit-coupling contributions.

Introduction

Cinchonine (cin = $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}$) belongs to the group of the four most important alkaloids of the *Cinchona* tree bark. Like the other members of this group, it is a biologically active compound and has an antimalarial activity comparable to that of quinine.⁴ The conformation of quinine molecule has been recently described for its derivative 10-hydroxy-10-methyl-10,11-dihydroquinine,⁵ while the absolute configuration of cinchonine (Figure 1) was determined in the course of the X-ray structure analysis of cinchoninium tetrachlorocadmate(II) dihydrate,⁶ which is one of the isomorphous compounds of the general formula $\text{cin} \cdot 2\text{HCl} \cdot \text{MCl}_2 \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Cd}, \text{Co}, \text{Zn}, \text{Hg}$).^{6,7} Their crystalline structure consists of M ions tetrahedrally surrounded by chlorine anions that form a system of hydrogen bonds with nitrogen atoms of $(\text{cinH}_2)^{2+}$ cations and with water molecules. This can be interpreted as a weak indirect interaction of M with cinchonine, as suggested by IR data.⁷ The MCl_4^{2-} complexes are well separated one from another in the crystal. Thus no magnetic or superexchange couplings between

Co(II) ions were detected by EPR⁸ and magnetic susceptibility⁹ in $(\text{cinH}_2)(\text{CoCl}_4) \cdot 2\text{H}_2\text{O}$.

The fact that the compound with $\text{M} = \text{Cu}$ is not isomorphous with the above series prompted us to perform X-ray diffraction, magnetic, EPR, and UV-vis studies on this compound as well as a detailed analysis of the electronic structure of CuCl_4^{2-} complexes in the crystalline state.

Experimental Section

Preparation of the Compound. Bis[cinchoninium tetrachlorocuprate(II)] trihydrate was prepared according to Dyrek's method.⁷ A solution of 10 mg of cinchonine (Koch-Light) in 60 mL of HCl (1:1) was mixed with 50 mL of CuCl_2 (0.5 M). The color of the solution changed rapidly from blue to green. The solution was heated for about 0.5 h on a water bath. After the solution was allowed to stand and cool, well-shaped greenish yellow crystals deposited. The crystals were filtered, washed with ethanol, and dried in the air. The crystals with a prismatic habit were elongated along the c -axis with well-developed (010) faces.

Crystal Structure Determination. The lattice parameters, determined together with other crystal data,¹⁰ were confirmed and refined in the autoindexing procedure from the setting angles of 15 reflections. The intensities of reflections were measured with a four-circle automatic CAD-4 Enraf Nonius diffractometer. The crystal and data collection

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