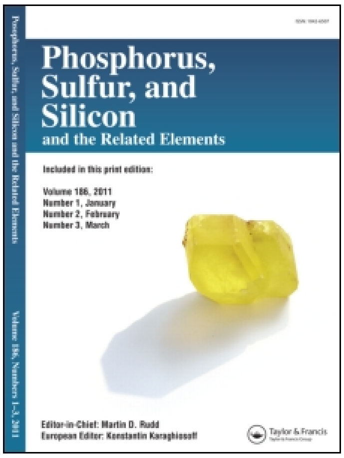

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Reactions of 1,1-Diiodo-3,4-benzocyclopentatellurane with Sulfur and Selenium Ligands: X-Ray Structure of a Dicationic Telluraheterocycle, $[C_8H_8Te\{S{=}C(NMe_2)_2\}_2][BF_4]_2$

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REACTIONS OF 1,1-DIIODO-3,4-BENZOCYCLOPENTATELLURANE WITH SULFUR AND SELENIUM LIGANDS: X-RAY STRUCTURE OF A DICATIONIC TELLURAHETEROCYCLE, $[C_8H_8Te\{S{=}C(NMe_2)_2\}_2][BF_4]_2$

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1,1-Diiodo-3,4-benzocyclopentatellurane, $C_8H_8TeI_2$, was reacted with a series of neutral thioureas, selenoureas, and thiones (L) in tetrahydrofuran in the presence of silver tetrafluoroborate to give dicationic complexes of the type $[C_8H_8Te(L)_2][BF_4]_2$. These have been characterized by multinuclear NMR spectroscopy, elemental analysis, and a representative single crystal X-ray structure for the complex with L = tetramethylthiourea. The structure and bonding are discussed and compared with related coordinated cyclopentatelluranes.

Keywords Heterocycle; NMR; tellurium; thiourea; X-ray structure

INTRODUCTION

The coordination chemistry of tellurium(IV) is a fascinating area of research, given the wide range of structural geometries shown and the type of ligands that bond to tellurium as the central atom. Eight is generally considered to be the maximum coordination number for tellurium (IV),[1] and this is reserved for complexes of the type TeL_4 [L = bidentate dithiocarbamates]. A coordination number of seven is also common when one of the ligands is replaced with a monodentate ligand (e.g., a halide, or an organic group—phenyl, etc). Typically, halogens, thio/selenoureas and anionic dithiocarbamates, dithiophosphates, and xanthates have been used in preparing and characterizing (organo)tellurium(IV) complexes. Of particular interest has been evidence of the stereochemically active lone pair on tellurium (IV).[2] In contrast, some of the higher coordination numbers (six or above) also have a tellurium atom that displays no evidence for a stereochemical lone pair: Archetypal examples

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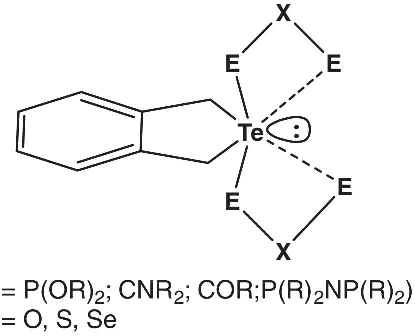


Figure 1 The general structures of organotellurium (IV) compounds discussed, typically showing one short (solid) and one long (dashed) Te-E bond.

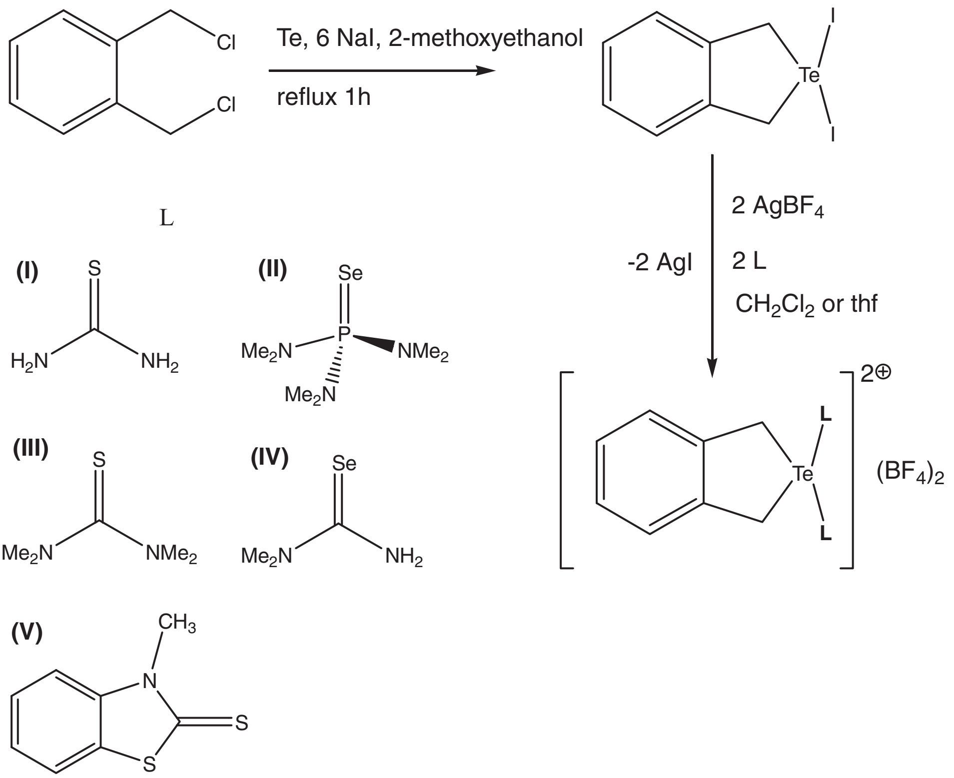
include TeX_6^{2-} [X = Cl, Br],[3,4] $TeX_4(tmtu)_2$ [tmtu = tetramethylthiourea],[5] and TeL_4 compounds such as Te(dithiocarbamate)$_4$. All of these examples show no intramolecular secondary bonding. However, the large array of structural variation in tellurium coordination arises from its tendency to participate in both inter- and intramolecular bonds, often of the Te···S type. As is commonly the case, and as outlined in the description and comparisons of the structures in this article, the bonding in dithiocarbamates, xanthates, and dithiophospates (among others) is unsymmetrical with one shorter and one longer Te···S bond (anisobidentate, Figure 1).

A survey of the literature reveals that several coordination compounds of the benzocyclopentatellurane (C_8H_8Te) fragment are known,[6–8] and all of them prepared through metathesis reactions from the readily accessible starting material, $C_8H_8TeI_2$.[9,10] These reports are dominated by the inclusion of anionic ligands such as (alkyl)dithiocarbamates, dithiophosphates,[11–15] and imidotetraphenyldithiodiphosphinate,[16] which have been a favorite in various structural coordination sphere investigations of selenium and tellurium during recent years. As part of our continued work in the coordination of neutral thioureas, selenoureas, and thiones with tellurium (II) and (IV),[17] we report in this article the synthesis of ionic benzocyclopentatelluranes with these sulfur- and selenium-containing molecules. To our knowledge, these novel compounds represent the first reported structurally characterized derivatives of cationic benzocyclopentatellurane. The in situ–generated $[C_8H_8Te][BF_4]_2$ species is a useful synthon in the preparation of main group and transition metal organotellurium compounds, and we are presently working to develop its chemistry.

RESULTS AND DISCUSSION

Preparation

The addition of two equivalents of silver tetrafluoroborate to a methylene chloride solution of 1,1-didiodobenzocyclopentatellurane results in the rapid formation of a precipitate of silver iodide, and a slight color change from yellow to yellow-orange as the dicationic $[C_8H_8Te]^{2+}$ species is produced in situ. Solutions of thioureas and selenoureas dissolved in dry and oxygen-free tetrahydrofuran or methylene chloride reacted upon addition to the dication, resulting in orange solutions (Scheme 1). These solutions were filtered using a syringe filter under argon to remove light-sensitive silver iodide; concentration of the solutions and subsequent cooling led to the formation of crystalline solids that were



Scheme 1 Synthesis of compounds and structures of the ligands used.

collected. The solids appear to be relatively stable at room temperature once out of the solvent, although they were kept under an inert atmosphere. After a period of 2–3 weeks, a slight gray deposit (presumably metallic selenium) was noted in compound **IV**.

Spectroscopy and Structure

The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ and showed the features that were expected; signals of the ligands and the tellurocycle were observed, although there were small shifts noted in the coordinated ligands as compared to the unbound ligands. This information is summarized in Table I. As is expected, all the compounds showed typical ^{11}B and ^{19}F NMR chemical shifts associated with the BF_4 anion (ca. -1 ppm[18] and -152 ppm,[19] respectively).

As was reported in recent work from this laboratory (and others),[17,20] upfield shifts of ca 3–10 ppm are seen in the ^{13}C NMR spectrum for the $C{=}S$ and $C{=}Se$ linkage of the compounds reported. The ^{31}P NMR for **II** exhibits a singlet at 65.5 ppm with $J(^{31}P\text{-}^{77}Se)$ 657 Hz, again similar to that reported in the $[(Me_2N)_3PSe\text{-}I]I_3$ complex, which shows a significant (ca. 20 ppm) downfield shift and decrease (ca. 200 Hz) in the coupling constant.[21] The IR spectra show the expected bands associated with the tellurium-containing organic ring and the coordinated ligands.[17,20] Interestingly, the chemical shift of the CH_2 protons

Table I ^{1}H and ^{13}C NMR of the synthesized compounds

Compound	^{1}H NMR	^{13}C NMR	^{31}P NMR	Important IR bands (intensity) (cm^{-1})
I	2.66 (s, br, 8H [S=C(NH_2)$_2$]$_2$, 4.76 (s, 4H, Te-CH$_2$), 7.36–7.48 (m, 4H C$_6$H$_4$)	56.5 (Te-CH$_2$), 128.5, 130.6, 138.3 (Arom *C*), 175.5 [S=*C*(NH$_2$)$_2$]$_2$	—	3362 (s), 3163 (s), 2970 (m), 2921 (m), 1480 (m), 1383 (m), 800 (w), 742 (w)
II	2.62 (d, 36H, J_{PH} = 12 Hz, [Se=P(NMe_2)$_3$]$_2$, 4.88 (m, 4H, Te-CH$_2$), 7.31–7.44 (m, 4H C$_6$H$_4$)	40.9 (d, J_{PC} = 18Hz [Se=P(NMe_2)$_3$]$_2$), 54.6 (Te-CH$_2$), 128.3, 130.9, 138.6 (Arom *C*)	65.5 [*J*(^{31}P-^{77}Se) 657Hz]	2941 (m), 1290 (m), 1154 (m), 1050 (w), 975 (m), 737 (m), 675 (w), 649 (m)
III	3.27 (s, 24H, [S=C(NMe_2)$_2$]$_2$, 4.99 (m, 4H, Te-CH_2), 7.36–7.45 (m, 4H C$_6$$H_4$)	43.9 [S=C(NMe_2)$_2$]$_2$, 57.7 (Te-*C*H$_2$), 128.4, 130.0, 138.5 (Arom *C*), 177.1 [S=*C*(NMe$_2$)$_2$]	—	2942 (m), 2812 (m), 1569 (m), 1445 (m), 1385 (s), 1314 (s), 798 (w), 743 (w)
IV	4.89 (m, 4H, Te-CH$_2$), 7.30–7.39 (m, 4H C$_6$H$_4$)	38.7, 42.1 (2s) Se=C(NH$_2$)(NMe_2)]$_2$, 56.1 (Te-*C*H$_2$), 128.3, 130.9, 138.1 (Arom *C*), 171.1 [Se=*C*(NH$_2$)(NMe$_2$)]$_2$	—	3340 (w), 3280 (w), 3164 (m), 2943 (m), 2855 (m), 1615 (s), 1359 (m), 840 (w)
V	3.66 (s, 6H, N-CH_3), 4.70 (m, 4H, Te-CH$_2$), 7.17–7.51 (m, 12H C$_6$H$_4$)	30.4 (N-*C*H$_3$), 52.3 (Te-*C*H$_2$), 113.8, 121.6, 125.7, 127. 3, 128.0, 130.3, 130.8, 138.6, 142.0 (Arom *C*), 180.0 [S=*C*-benzothiazole)]	—	2943 (m), 1348 (m), 1125 (m), 950 (w), 804 (m)

^{11}B NMR: **I**—1.6 ppm; **II**—1.3 ppm; **III**—1.1 ppm; **IV**—1.5 ppm; **V**—1.6 ppm (all at 25°C).
^{19}F NMR: **I**—152.6 ppm; **II**—152.2 ppm; **III**—152.6 ppm; **IV**—152.2 ppm; **V**—152.8 ppm (all at 25°C).

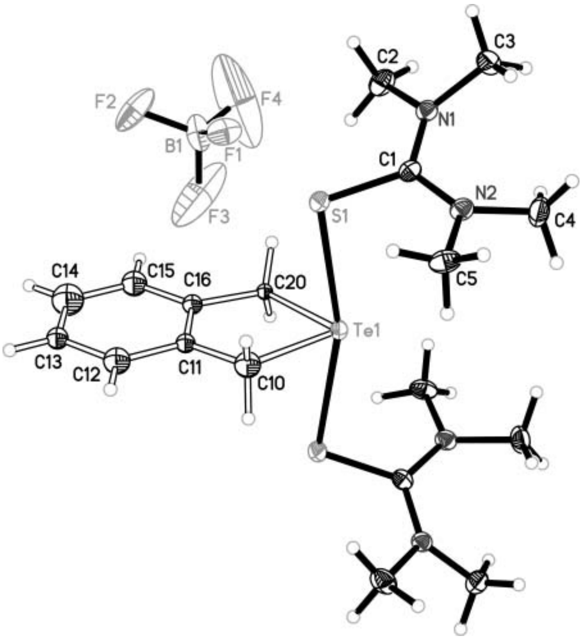


Figure 2 X-ray Structure of (III) at the 30% probability level, showing the dication and one of the tetrafluoroborate anions

of the telluracyclopentane ring [adjacent to the Te(IV) center] are considerably shifted downfield compared to those reported with anionic ligands.[6,8]

Crystal and Molecular Structure of [C_8H_8Te(tetramethylthiourea)$_2$] [BF_4]$_2$ (III)

The molecular structure of **III** with the atom numbering scheme is shown in Figure 2, and selected interatomic distances and bond angles are listed in Table II.

In accordance with valence shell electron pair repulsion theory,[22] the molecule displays an approximately ψ-trigonal bipyramidal geometry with one equatorial position

Table II Important interatomic distances (Å) and bond angles (°) for [C_8H_8Te(tmtu)$_2$][BF_4]$_2$ **(III)**

Te1-C10	2.122(12)	S1-Te1-S1	163.36(6)
Te1-C20	2.158(10)	C1-S1-Te1	100.29(16)
Te1-S1	2.6522(12)	C1-N1-C3	123.6(4)
S1-C1	1.746(5)	C1-N1-C2	122.7(4)
N1-C1	1.322(6)	C3-N1-C2	113.4(4)
N1-C3	1.465(7)	C1-N2-C5	123.0(4)
N1-C2	1.467(6)	C1-N2-C4	122.4(4)
N2-C1	1.342(6)	C5-N2-C4	114.2(4)
N2-C5	1.466(6)	N1-C1-N2	120.9(4)
N2-C4	1.469(7)	N1-C1-S1	119.6(4)
C10-C11	1.454(15)	N2-C1-S1	119.5(4)
		C11-C10-Te1	107.0(8)

occupied by a stereochemically active lone pair of electrons [sawhorse structure, typical of Te(IV)],[23] two equatorial bonds to C (organic), and two approximately linearly sulfur-coordinated tetramethylthiourea ligands.

Upon examination of the structure, it can be see that the organic C_8H_8 moiety is bonded to Te in an approximately symmetrical fashion with Te-C bond lengths of 2.122(12) and 2.158(10) Å. These bond distances are close to those reported previously in the starting material, $C_8H_8TeI_2$, and in the dithiocarbamate complex, $C_8H_8Te(Etdtc)_2$. A comparison of important geometrical parameters of closely related compounds is shown in Table III. This is the first example of a sulfur-coordinated telluracycle that does not contain a long secondary Te$\cdots\cdots$S bond: In the literature examples indicated in Table III, the dithio ligands (dialkyldithiocarbamates, xanthates, and phosphates) are all anisobidentate containing one short [ca. 2.5 Å] and one longer [>3.2 Å] bond distance. In the previous examples, the long Te-S bonds are found in the faces of the trigonal bipyramid, giving the tellurium atom an effective coordination number of seven. Claxton and Benson describe this as a 1:2:2:2 geometry.[24]

The tellurium atoms lies a small distance (0.056 Å) out of the plane of the 8 carbons of the C_8H_8 group and is in line with other deviations observed.[7] The interplanar angle described by the two planes C10-C20-Te1 and the S1-N1-N2-C1 (thiourea) is 33.09°, which is close to that reported in the related T-shaped tellurium (II) compound [Naph-TeBr(tetramethylthiourea)][20] in which the equivalent interplanar angle is 28.73°, thereby showing a very similar twist. Important torsion angles in **III** include Te(1)-S(1)-C(1)-N(1) at 23.11° and Te(1)-S(1)-C(1)-N(2) at 178.74°. Compound **III** is unique in that it represents a true monodentate (rather than an anisobidentate) ligand coordinated to the C_8H_8Te fragment that has been structurally characterized for the first time; however, just as the structures described in Table III contain "long" Te$\cdots$S interactions, so **III** shows a long contact between Te(1) and F(2) of the tetrafluoroborate counteranion. The bond length is 3.249 Å (somewhat less than the sum of the van der Waals radii at 3.53 Å[25]); interestingly enough, the bond angle subtended between F(2)-Te(1)-S(2) is 77.00(10)°, and lies somewhat above those observed for the anisobidentate sulfur ligands of dithiocarbamates, xanthates, and dithiophosphates. For example, in $C_8H_8Te(Etdtc)_2$, a S-Te-S bite angle from the "long" bond to the "short" bond of close to 60° is seen for both ligands. (This "long" sulfur is the one that is thought of as forming the facial intersections on the trigonal bipyramid.)

A somewhat unusual structure is presented in the mixed valent tellurium (IV)–tellurium (VI) compound $Te^{(VI)}[OTe^{(IV)}(C_8H_8)(S_2P(OEt)_2)]_6$ with its essentially ocahedral Te core surrounded by six $[OTe(C_8H_8)(S_2P(OEt)_2]$ groups.[26] Again, there is an anisobidentate dithiophosphate ligand coordinated to the Te center, but with a Te-O bond and a long Te-S interaction [from a sulfur of an adjacent diethyldithiophosphate—and hence closely related to $[C_8H_8Te(Etdtp)_2]$. Related compounds including a non-aromatic C_4H_8Te heterocycle are included in Table III.[27] There is also a series of reported "half-metathesized" compounds in which one of the halogens in the $C_8H_8TeI_2$ starting material has been replaced with the usual type of ligand. We were unable to isolate any mixed complexes of the type $[C_8H_8TeI(L)]BF_4$ in the course of our investigations, even with careful control over the stoichiometry of the reaction (one equivalent of ligand and one equivalent of silver tetrafluoroborate). A detailed discussion of the geometrical parameters of those structures is not warranted here, but they include the following synthesized compounds: $[C_4H_8TeI\{Ph_2P(Se)PNP(Se)Ph_2\}]$ and $[C_4H_8TeI\{imdd\}]$,[28] $[C_8H_8TeI\{S_2PR_2\}]$ (R = Me, Et),[29] and $[C_8H_8TeI(Etdtc\}]_2$.[30]

Table III A comparison of structural parameters (bond distances and angles) in **III** and related compounds

Compound	Te-C length (Å)	Te-S length (Å) short/[long] *Ligand abbreviation*		X-Te-X angle (°)	Reference
$C_8H_8TeI_2$	2.136(8)	—		179.53(3)	10
$C_8H_8Te(Etdtc)_2$	2.150(4)	2.599(1);	2.622(1)/	168.55(4)	6
	2.143(2)	[3.220(1);	3.270(1)]		
		Etdtc;	*Etdtc*		
$C_8H_8Te(Etxan)_2$	2.125(2)	2.6142(7);	2.6410(7)/	164.63(2)	6
	2.143(2)	[3.3440(7);	3.2720(6)]		
		Etxan;	*Etxan*		
$C_8H_8Te(Etdtp)_2$	2.133(11)	2.627(4);	2.621(3)/	163.6(1)	6
	2.109(9)	[3.493(4);	3.447(4)]		
		Etdtp;	*Etdtp*		
$Te^{(VI)}[OTe^{(IV)}(C_8H_8)(S_2P(OEt)_2)]_6$	2.127(13)	2.691(4);	2.051(7)/	168.2(2)	25
	2.140(13)	3.477(6);	3.569(5)		
		Etdtp;	*Te-O/Te-S*		
$[C_8H_8Te(tmtu)_2][BF_4]_2$	2.122(12)	2.6522(12)		163.36(6)	**This work**
	2.158(10)	*tmtu*			
$C_8H_8Te(OAc)_2$	2.104(4)	2.216(3);	2.100(3)/	162.0(1)	7
	2.117(4)	[2.989(3);	2.903(5)]		
		Bonds to acetate oxygen			
$C_8H_8Te(Etdtc)(Etdtp)$	2.139(5)	2.521(1);	2.742(2)/	171.75(5)	7
	2.158(5)	[3.103(2);	3.438(8)]		
		Etdtc;	*Etdtp*		
$C_8H_8Te(Etdtc)(itdd)$	2.134(7)	2.538(2);	2.760(2)/	161.55(7)	8
	2.129(7)	[3.150(2);	3.303(2)]		
		Etdtc;	*itdd*		
$C_8H_8Te(pipdtc)(itdd)$	2.140(7)	2.521(2);	2.773(2)/	167.95(7)	8
	2.138(6)	[3.188(2);	3.307(2)]		
		pipdtc;	*itdd*		
$C_8H_8Te(tmorphdtc)(imdd)$	2.143(6)	2.530(2);	2.783(2)/	168.55(5)	8
	2.161(6)	[3.149(2);	3.343(2)]		
		tmorphdtc;	*itdd*		
$C_8H_8Te(pipdtc)_2$	2.151(7)	2.610(2)	2.707(2)/	164.76(6)	29
	2.147(6)	3.046(2)	3.166(2)		
		pipdtc			
$C_4H_8Te(imdd)_2$	2.152(7)	2.670(2);	2.643(2)/	170.59(5)	28
	2.153(6)	[3.300(2);	3.451(2)]		
		itdd			
$C_4H_8Te[S_2P(OCH_2)_2CMe\text{-}^{n}Pr]_2$	2.133(7)	2.6410(8)/		174.61(10)	27
		[3.495(2)]			
		MePrethdtp			
$C_4H_8Te[S_2P(OCH_2)_2CEt_2]_2$	2.154(7)	2.683(2);	2.553(2)/	174.08(9)	27
	2.155(7)	[3.381(3);	3.380(3)]		
		Etethdtp;	*Etethdtp*		
NapthTeBr(tmtu)	2.169(5)	2.5930(11)		171.14(3)	20
		tmtu			

Abbreviations: Etdtc = ethyl dithiocarbamate; Etdtp = ethyl dithiophosphate; Ac = acetate; itdd = iminotetraphenyldithiodiphosphinate; Etxan = ethyl xanthate; MePrethdtp = $S_2P(OCH_2)_2CMe\text{-}^{n}Pr$; Etethdtp = $S_2P(OCH_2)_2CEt_2$; tmtu = 1,1,3,3-tetramethylthiourea; tmorphdtc = thiomorpholinodithiocarbamate; pipdtc = piperidinyl dithiocarbamate; Etethdtp = $S_2P(OCH_2)_2CEt_2$.

EXPERIMENTAL

All experiments were conducted under an atmosphere of argon gas using conventional Schlenk/vacuum line techniques. All solvents were dried according to reported methods.[31] 1,1-Diiodobenzocyclopentatellurane was prepared according the method of Ziolo and Günther[9]; the ligands and silver tetrafluoroborate were purchased from Aldrich Chemical Co. and were used as received. NMR spectra were recorded on a Bruker AX-250 (^{1}H NMR recorded at 250 MHz, ^{13}C NMR recorded at 62.9 MHz) using $CDCl_3$ and TMS as an internal standard. IR spectra were recorded on a Nicolet Avatar 360 FT-IR spectrometer using KBr discs. Elemental analyses were performed at Atlantic Microlab Inc. (Norcross, GA, USA).

General Synthesis of $[C_8H_8Te(L)_2][BF_4]_2$

A Schlenk flask was charged with 1,1-diiodocyclopentatellurane (0.200 g, 0.412 mmol), and dry methylene chloride (10 mL) was added via a syringe. The solution was stirred until all the starting material had dissolved. Silver tetrafluoroborate (0.160 g, 0.824 mmol) was added, forming an immediate white precipitate in a yellow-orange solution. After 5 min, a solution of the ligand (2 molar eq) dissolved in methylene chloride (10 mL) was added via syringe, and the reaction was stirred at room temperature for 1 h. It was filtered via a syringe filter and concentrated to ca. 5 mL volume. Upon cooling to −20°C overnight in a freezer, small yellow to orange microcrystals were formed. X-ray diffraction quality crystals were grown by vapor diffusion of pentane into a methylene chloride solution (for **III**). Table IV indicates the physical properties of compounds **I**–**V**, while Table I describes the IR and selected NMR data. The quantities used are given below.

$[C_8H_8Te(thiourea)_2][BF_4]_2$ (I). 1,1-Diiodocyclopentatellurane (0.500g, 1.03 mmol), thiourea (0.156 g, 2.06 mmol), and $AgBF_4$ (0.400 g, 2.06 mmol) were combined as described. A yellow-orange solution formed that was concentrated to 3 mL. In a freezer, overnight, light yellow microcrystals formed. Yield: 0.37 g, 65%.

$[C_8H_8Te(tris\{dimethylamino\}phosphane\ selenide)_2][BF_4]_2$ (II). 1,1-Diiodocyclopentatellurane (0.200 g, 0.412 mmol), tris{dimethylamino}phosphane selenide (0.200 g, 0.810 mmol), and $AgBF_4$ (0.161 g, 0.830 mmol) were combined as

Table IV Physical and analytical data for compounds I–V

Compound	Formula (mol. wt.)	Melting point (°C)	Color	Elemental analysis: Calcd. (Found) C	H	N
I	$C_{10}H_{16}B_2F_8N_4S_2Te$ (557.6)	151–153	Yellow	21.54 (21.66)	2.89 (2.95)	10.05 (9.97)
II	$C_{20}H_{44}B_2F_8N_6P_2Se_2Te$ (889.7)	102–104	Orange	27.00 (27.12)	4.99 (5.09)	9.45 (9.46)
III	$C_{18}H_{32}B_2F_8N_4S_2Te$ (669.8)	180–182	Yellow	32.28 (32.44)	4.82 (4.69)	8.36 (8.29)
IV	$C_{14}H_{24}B_2F_8N_4Se_2Te$ (707.5)	90 (dec)	Yellow-orange	23.77 (23.98)	3.42 (3.46)	7.92 (7.88)
V	$C_{24}H_{22}B_2F_8N_2S_4Te$ (767.9)	199–201	Yellow	37.54 (37.51)	2.89 (2.80)	3.65 (3.71)

described. A yellow-orange solution formed that was concentrated to 5 mL. In a freezer, overnight, bright yellow microcrystals formed. Yield: 0.27 g, 75%.

[C_8H_8Te(tetramethylthiourea)$_2$][BF_4]$_2$ (III). 1,1-Diiodocyclopentatellurane (0.400 g, 0.82 mmol), 1,1,3,3-tetramethylthiourea (0.216 g, 1.64 mmol), and $AgBF_4$ (0.320 g, 1.64 mmol) were combined as described. An orange solution formed that was concentrated to 3 mL. In a freezer, overnight, light yellow microcrystals formed. Yield: 0.40g, 70%. Vapor diffusion of pentane into a methylene chloride (0.5 mL) solution of **III** led to X-ray quality yellow block crystals.

[C_8H_8Te(N,N′-dimethylselenourea)$_2$][BF_4]$_2$ (IV). 1,1-Diiodocyclopentatellurane (0.200 g, 0.412 mmol), N,N′-dimethylselenourea (0.124 g, 0.84 mmol), and $AgBF_4$ (0.160 g, 0.824 mmol) were combined as described. A yellow-orange solution formed that was concentrated to 2 mL. In a freezer, overnight, light orange microcrystals formed. Yield: 0.21 g, 73%.

[C_8H_8Te(N-methylbenzothazol-2(3H)-thione)$_2$][BF_4]$_2$ (V). 1,1-Diiodocyclopentatellurane (0.200 g, 0.412 mmol), N-methylbenzothazol-2(*3H*)-thione (0.149 g, 0.84 mmol), and $AgBF_4$ (0.160 g, 0.824 mmol) were combined as described. An orange solution formed that was concentrated to 2 mL. In a freezer, overnight, light orange microcrystals formed. Yield: 0.19 g, 66%.

Structure Determination

Crystal data and structure refinement parameters are shown in Table V. Crystallographic data were collected on a crystal with dimensions 0.23 × 0.23 × 0.16 mm for **III**. Data were collected at 120 K on a Bruker Apex2 CCD diffractometer using CuKα radiation

Table V Structure refinement details for **III**

Empirical formula	$C_{18}H_{32}B_2F_8N_4S_2Te$
Formula weight	669.82
Crystal system/space group	Orthorhombic/Pbcn
a/Å	15.9028(3)
b/Å	11.7641(2)
c/Å	13.9027(3)
α/Å	90
β/Å	90
γ/Å	90
V/Å^3	2600.95(9)
Z	4
D $_{calc}$ (g/cm^3)	1.711
μ (mm^{-1})	11.202
Crystal size (mm)	0.23 × 0.23 × 0.16
Color/Shape	Yellow/block
Temp (K)	120(2)
Theta range for collection	4.68 to 61.47
Reflections collected	21483
Independent reflections	2002
Data/restraints/parameters	2002/0/143
Goodness of fit on F^2	1.034
Final R indices [I > 2σ(I)]	$R1 = 0.0441$ w$R2 = 0.0991$
R indices (all data)	$R1 = 0.0454$ w$R2 = 0.0982$
Largest difference peak/hole	2.182/−1.490 e/A^3

($\lambda = 1.54178$ Å). The structure was solved by direct methods after absorption correction of the data using SADABS.[32] All of the data were processed using the Bruker suite of software (XS/SHELXTL/SHELX-97).[33] The dication is positioned on a two-fold axis (through the Te atom), and there are two tetramethylthiourea ligands and two counteranions. The aromatic ligand appears to be disordered around a two-fold axis; a speculative reason for this may be that the cage formed by the two tetramethylthiourea ligands and the additional Te···F contacts is too big, and the aromatic group librates from one wall to another. This is a possible reason for the degeneration of symmetry. All H-atoms were put in calculated positions with coordinates riding on pivotal atoms. For the CH_3 groups of tetrammethylthiourea, this torsion angle was refined. The residual electron density of ca 2e/Å^3 relates to a possible additional disorder of the BF_4^- anion that was not resolved.

Supplementary Information

Crystallographic data for the structural analysis of compound **III** has been deposited at the Cambridge Crystallographic Data Center (CCDC number 624550). Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44–1223-336033; email: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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