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Article

Heavy Atom Analogues of 1,2,3-Dithiazolylium Salts: Preparation, Structures and Redox Chemistry

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Synthetic routes to salts of the benzo[1,2,3]thiatellurazolylium cation [**2c**]$^+$ and its selenium analogue [**2b**]$^+$ are described. Access to the cation frameworks involves the intermediacy of *N,N,S*-trisilylated 2-aminobenzenethiol. The latter reacts smoothly with selenium and tellurium halides ECl_4 (E = Se, Te) to afford the desired heterocyclic benzo cations [**2b**]$^+$ and [**2c**]$^+$ as their chloride salts. Anion exchange provides the corresponding $GaCl_4^-$, OTf^- and $TeCl_5^-$ salts of [**2c**]$^+$, all of which have been characterized by X-ray crystallography. While the gallate salts of the sulfur and selenium cations [**2a**]$^+$ and [**2b**]$^+$ crystallize as ion-paired cations and anions, salts of [**2c**]$^+$ adopt solid-state structures that display strong association of the cations via short intermolecular Te−N′ bonds. However, crystallization of [**2c**]$^+$ salts in dichloroethane in the presence of $GaCl_3$ leads to cleavage of the dimers and the formation of a Lewis acid adduct at nitrogen. Reduction of the benzo cations [**2a**,**b**]$^+$ affords the respective radicals **2a**,**b**, both of which have been characterized by electron paramagnetic resonance (EPR) spectroscopy. Attempts to generate the corresponding radical **2c** have been unsuccessful, although a material of nominally correct elemental composition can be generated by chemical reduction. The energetics of association of [**2a**,**b**,**c**]$^+$ in solution has been probed by means of density functional theory calculations using the polarized continuum model. The results suggest that the dimeric nature of the Te-centered cation is retained in solution. The strength of the interaction is, however, less than in *N*-alkylated tellurodiazolylium salts.

Introduction

There is increasing interest in the use of heavy atom heterocyclic radicals as building blocks for the design of molecular materials exhibiting conductive and magnetic properties.[1] Within this context we have recently demonstrated that replacement of sulfur in resonance stabilized bisdithiazolyls by its heavier congener selenium can lead not only to enhanced conductivity[2] but also to dramatic magnetic effects, including spin-canted antiferromagnetism[3] and even bulk ferromagnetism.[4] These findings prompt the question as to whether the incorporation of tellurium into chalcazyl radicals will further enhance transport properties. However, while there is extensive literature on the chemistry and structures of unsaturated organic[5,6] and inorganic[7] heterocycles containing tellurium-nitrogen linkages, there are no reports of the isolation or even observation of a neutral radical akin to those seen for heterocycles containing SN and SeN linkages.

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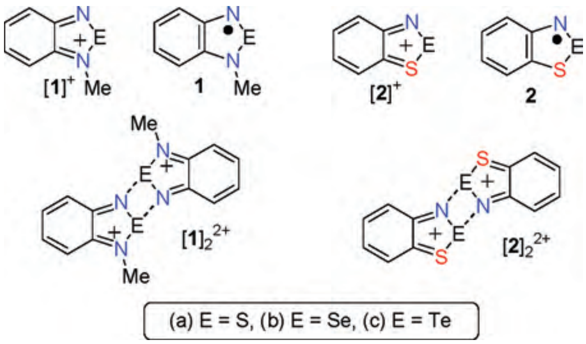
Chart 1



In order to explore the potential of tellurazyl radicals, we are pursuing the synthesis and characterization of new families of cationic heterocycles which might, upon reduction, afford radical species. To this end, we recently carried out a comparative study of the structures and redox chemistry of the family of *N*-methylated benzochalcodiazolylium cations [**1a**,**b**,**c**]$^+$ (Chart 1).[8] While the triflate salt [**1a**][OTf] (OTf^- = triflate) crystallized as discrete [**1a**]$^+$ cations and OTf^- anions, the corresponding triflates of [**1b**]$^+$ and [**1c**]$^+$ consisted of centrosymmetric dimers [**1b**]$_2^{2+}$ and [**1c**]$_2^{2+}$. The closeness of the intermolecular E$-$N′ contacts suggested strong association, especially for E = Te. The sulfur and selenium cations [**1a**,**b**]$^+$ could be reduced, both chemically and electrochemically, to the corresponding radicals **1a**,**b**, which were characterized by electron paramagnetic resonance (EPR) spectroscopy. However, the electrochemical behavior of the tellurium cation [**1c**]$^+$ was very different, both in terms of half-wave potentials and reversibility, and no EPR signal corresponding to **1c** could be generated. Collectively, the results led us to suggest that the association of [**1c**]$^+$ observed in the solid state was maintained in acetonitrile solution, in which case one-electron reduction of [**1c**]$_2^{2+}$ would afford not the neutral radical **1c** but a dimer radical cation [**1c**]$_2^+$.

In order to explore the generality of these findings, in particular the degree of association of heterocyclic tellurium-nitrogen cations in both the solid state and in solution, we have turned our attention to the family of benzochalcazolylium cations [**2a**,**b**,**c**]$^+$ and the corresponding radicals **2a**,**b**,**c**. While the all-sulfur cation [**2a**]$^+$ and radical[9] have been known for many years, the selenium centered cation [**2b**]$^+$ has received only passing attention,[10] and radical **2b** has never been observed. Most importantly there is no mention in the literature of the tellurium based cation [**2c**]$^+$, let alone the corresponding radical **2c**. Herein we report the preparation and structural characterization of the three cations [**2a**,**b**,**c**]$^+$. In the case of [**2c**]$^+$, the structures of several salts are described. While dimerization of [**2c**]$^+$ is observed in all cases, the length of the interdimer Te$-$N′ interactions suggests that the strength of the association is less than that found in [**1c**]$^+$. The effect has been modeled by means of density functional theory (DFT) methods. The sulfur and selenium cations [**2a**,**b**]$^+$ undergo one-electron reduction to the corresponding radicals **2a**,**b**, which have been characterized by EPR spectroscopy. Attempts to generate the neutral radical **2c** are also described.

Results and Discussion

Synthesis. Aromatic 1,2,3-dithiazolylium salts are easily prepared by the Herz reaction, that is, the cyclization of an aromatic amine with sulfur monochloride.[11] This reaction is, however, often accompanied by chlorination of the aromatic ring.[12]

The latter complication can be avoided in the condensation of an *o*-aminothiol with thionyl chloride.[13] Thus, the reaction of benzene-aminothiol **3** with thionyl chloride affords [**2a**][Cl] in high yield (Scheme 1). This crude chloride salt can be converted into the more soluble gallate [**2a**][$GaCl_4$] by treatment with gallium trichloride. The same approach cannot be applied to the preparation of salts of the selenium cation [**2b**]$^+$, as complete elimination of 3 equiv of HCl cannot be effected. The condensation route can, however, be achieved if the amine and/or thiol groups are first acetylated.[14] Alternatively salts of [**2b**]$^+$ can be generated in a single step by heating salts of [**2a**]$^+$ with SeO_2 in acetic acid.[10a] Unfortunately, the latter route cannot be adapted for the preparation of [**2c**]$^+$, as TeO_2 does not react with dithiazolylium salts.

In order to generate the Te-containing ring [**2c**]$^+$ we sought a soft organometallic condensation reagent that would react cleanly with $TeCl_4$ and circumvent the HCl elimination problem noted above. To this end we prepared the *N*,*S*-disilylated derivative **4** by treatment of **3** with hexamethyldisilazane (HMDS) at reflux. Deprotonation of **4** and treatment of the intermediate amide with chlorotrimethylsilane afforded the *N*,*N*,*S*-trisilylated compound **5**, which

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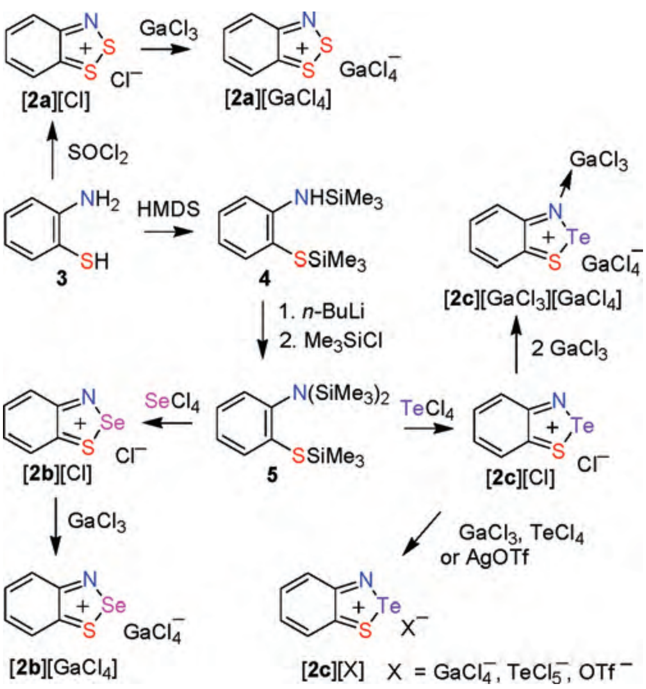
Scheme 1



reacted very cleanly with $SeCl_4$ in refluxing MeCN, and with $TeCl_4$ in refluxing dichloroethane (DCE), to produce the corresponding selenazolylium chloride [**2b**][Cl] and tellurazolylium chloride [**2c**][Cl]. As above, treatment of the crude chloride salts with $GaCl_3$ in MeCN afforded the gallates [**2b**,**c**][$GaCl_4$], which could be crystallized from chlorobenzene or DCE. A triflate salt [**2c**][OTf] was also prepared by metathesis of the chloride salt [**2c**][Cl] with silver triflate. In addition to [**2c**][$GaCl_4$] and [**2c**][OTf], two other salts of the tellurium cation were isolated. During early attempts to perform the reaction of **5** with $TeCl_4$ in MeCN at room temperature, a crystalline material was isolated that displayed a slightly different IR spectrum from that of [**2c**][Cl]. When treated with $GaCl_3$ in MeCN this material dissolved to afford a deep red solution, evaporation of which afforded crystals of the pentachlorotellurate salt [**2c**][$TeCl_5$]. In a second and somewhat surprising variation, when [**2c**][Cl] was treated with gallium trichloride in a noncoordinating solvent (DCE or liquid SO_2), evaporation of the solvent afforded extremely moisture-sensitive red plates of the *N*-coordinated Lewis acid adduct [**2c**][$GaCl_3$][$GaCl_4$] (δ ^{125}Te (DCE) = 1337 ppm). When redissolved in donor solvents, this complex appears to dissociate. A solution of [**2c**][$GaCl_3$][$GaCl_4$] in MeCN, for example, affords a ^{125}Te NMR signal with a chemical shift of 1429 ppm, which is virtually identical with that of pure [**2c**][$GaCl_4$] (δ ^{125}Te = 1427 ppm).[15]

Crystal Structures. In order to establish the solid-state structural preferences for the family of cations [**2a**,**b**,**c**]$^+$, we determined the crystal structures of their tetrachlorogallate salts [**2a**,**b**,**c**][$GaCl_4$]. In addition, and in order to explore the possible effects of different counterions on the degree of association of the tellurium based cation, we also characterized the two salts [**2c**][OTf] and [**2c**][$TeCl_5$] and the Lewis acid adduct salt [**2c**][$GaCl_3$][$GaCl_4$]. Crystallographic data are compiled in Table 1 and a summary of pertinent intra- and intermolecular distances is provided in Table 2. Representative views of the cation−anion pairs for all six structures are presented in Figures 1−4.

Yellow crystals of the parent benzodithiazolylium salt [**2a**][$GaCl_4$] belong to the orthorhombic space group $P2_12_12_1$, with four cations and four anions per unit cell. As in other simple 1,2,3-dithiazolylium salts,[16] the cations are well separated, and there is only one short cation−anion contact, that is, S1−Cl4′ (3.4077(13) Å) shown in Figure 1. Orange plates of the corresponding selenium salt [**2b**][$GaCl_4$] are not isomorphous; instead they belong to the monoclinic space group $P2_1/n$. However, as in the case of [**2a**][$GaCl_4$], the cations in [**2b**][$GaCl_4$] remain well separated, although they are linked to a $GaCl_4^-$ anion by a number of short contacts, including Se1−Cl2′ (3.2155(10) Å) and S1−Cl2′ (3.3861(14) Å) shown in Figure 1. The absence of cation association is notable, as in *N*-alkylated selenodiazolium salts such as [**6**][$GaCl_4$][17] and [**1b**][OTf][8] close centrosymmetric cation pairing is observed (Chart 2).[18] Also, while cation association is absent for the benzo-cation [**2b**]$^+$, addition of another aromatic ring, as in the naphthothiaselenazolylium salt [**7**][$GaCl_4$],[14] leads to association of the cations, although the Se−N′ contacts (2.874(4) Å) are lengthened. The energetics of these processes are explored below.

The crystal structures of the tellurium centered salts [**2c**][X] (X^- = $GaCl_4^-$, OTf^-, $TeCl_5^-$) all show the same basic structural features (Figures 2 and 3), that is, centrosymmetric pairing of cations [**2c**]$^+$ to form almost coplanar[19] dimer dications [**2c**]$_2^{2+}$ bridged by short intermolecular Te−N′ contacts of 2.5324(17) Å (X^- = $GaCl_4^-$), 2.538(2) Å (X^- = $TeCl_5^-$) to 2.553(4) Å (X^- = OTf^-). These are remarkably short, well within the normal van der Waals separation,[20] although slightly longer than those seen in the dimer [**1c**]$_2$[OTf]$_2$ (2.417(3) Å),[8] and significantly longer than in $[(Cl_2Te)_2N]_2[AsF_6]_2$, where the intra- and intermolecular Te−N bonds (1.98(4) Å and 2.04(4) Å respectively) are almost equivalent.[21] In addition, all the structures possess short cation−anion pairing contacts spanning the Te−S unit of the cation and a Cl atom (in $GaCl_4^-$ and $TeCl_5^-$) or an oxygen atom (in OTf^-). Collectively, the intramolecular bonds and intermolecular contacts to tellurium afford what can be described, in VSEPR parlance, as a pseudo square-

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(15) Attempts to observe a possible dimer-monomer equilibrium, that is, between [**2c**]$^+$ and [**2c**]$_2^{2+}$, by ^{125}Te NMR (in MeCN and DCE) have shown no evidence of a second species. Only one signal, which we ascribe to the dimer, is observed.

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(19) In [**2c**][$GaCl_4$], [**2c**][OTf] and [**2c**][$TeCl_5$] the two rings of the dimer dication straddle an inversion centre, so they must be parallel. The very slight departure from rigorous coplanarity of the two halves, most notable in the $TeCl_5^-$ derivative, is simply a result of crystal packing forces.

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Table 1. Crystal Data

compound	[**2a**][GaCl$_4$]	[**2b**][GaCl$_4$]	[**2c**][GaCl$_4$]	[**2c**][OTf]	[**2c**][TeCl$_5$]	[**2c**][GaCl$_3$][GaCl$_4$]
formula	$C_6H_4Cl_4GaNS_2$	$C_6H_4Cl_4GaNSSe$	$C_6H_4Cl_4GaNSTe$	$C_7H_4F_3NO_3S_2Te$	$C_6H_4Cl_5NSTe_2$	$C_6H_4Cl_7Ga_2NSTe$
M	365.74	412.64	461.29	398.85	554.61	637.35
a (Å)	8.6904(4)	7.4587(3)	7.7297(9)	12.0892(5)	8.2184(5)	9.7208(3)
b (Å)	9.6874(5)	10.2322(4)	9.7183(5)	12.0493(5)	8.2820(5)	18.2525(5)
c (Å)	14.6214(7)	17.0845(7)	9.8185(5)	7.9429(3)	11.0240(7)	9.9986(3)
α (°)			116.0530(10)		82.7070(11)	
β (°)		94.4450(10)	99.3900(10)	90.7930(10)	72.9321(12)	99.0130(10)
γ (°)			95.5220(10)		74.4782(12)	
V (Å^3)	1230.94(10)	1299.95(9)	641.90(9)	1156.90(8)	690.18(7)	1752.14(9)
ρ_{calcd} (g cm^{-1})	1.974	2.108	2.387	2.290	2.669	2.416
space group	$P2_12_12_1$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
Z	4	4	2	4	2	4
temp (K)	296(2)	296(2)	290(2)	290(2)	296(2)	200(2)
μ (mm^{-1})	3.401	5.860	5.326	2.966	5.313	5.874
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
data/restr/parameters	3597/0/129	3755/0/128	3849/0/128	3287/0/154	4067/0/136	5093/0/164
solution method	direct methods	direct methods	direct methods	direct methods	direct methods	direct methods
R, R_w (on F^2)	0.0270, 0.0600	0.0401, 0.0653	0.0201, 0.0473	0.0284, 0.0738	0.0221, 0.0539	0.0307, 0.0591

Table 2. Selected Distances[a] (Å)

	E−S	E−N	S−C	N−C	E−N′	δ[b]
[**2a**][GaCl$_4$]	2.0243(14)	1.561(3)	1.693(3)	1.345(4)		0.0080
[**2b**][GaCl$_4$]	2.1744(11)	1.740(3)	1.711(4)	1.324(4)		0.0235
[**2c**][GaCl$_4$]	2.3818(6)	1.9543(16)	1.702(2)	1.327(3)	2.5324(17)	0.0145
[**2c**][OTf]	2.3757(12)	1.949(4)	1.697(5)	1.330(5)	2.553(4)	0.0084
[**2c**][TeCl$_5$]	2.3881(8)	1.954(2)	1.698(3)	1.328(3)	2.538(2)	0.0258
[**2c**][GaCl$_3$][GaCl$_4$][c]	2.3407(9)	1.982(2)	1.703(3)	1.341(4)		0.0186

[a] Short intermolecular contacts: [**2a**][GaCl$_4$]: S1−Cl4′ 3.4077(13) Å (no other short contacts); [**2b**][GaCl$_4$]: Se1−Cl2′ 3.2155(10) Å, S1−Cl2′ 3.3861(14) Å; [**2c**][GaCl$_4$]: Te1−Cl2′ 3.2963(6), S1−Cl2′ 3.4709(8) Å; [**2c**][OTf]: Te1−O1′ 2.880(4), S1−O1′ 3.008(4) Å; [**2c**][TeCl$_5$]: Te1−Cl5′ 3.3749(9), S1−Cl4′ 3.4565(14) Å; [**2c**][GaCl$_3$][GaCl$_4$]: Te1−Cl2′ 3.1633(8), S1−Cl2′ 3.3019(13) Å. [b] Mean deviation from plane (Å) for cation. [c] Ga1−N1 2.011(3) Å.

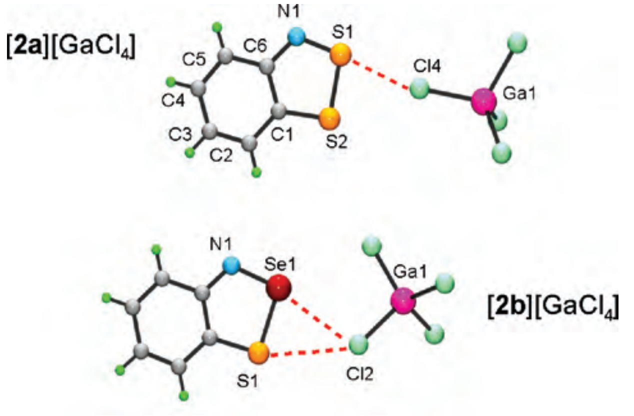

Figure 1. Single ion pairs of [**2a**][GaCl$_4$] and [**2b**][GaCl$_4$], with atom numbering.

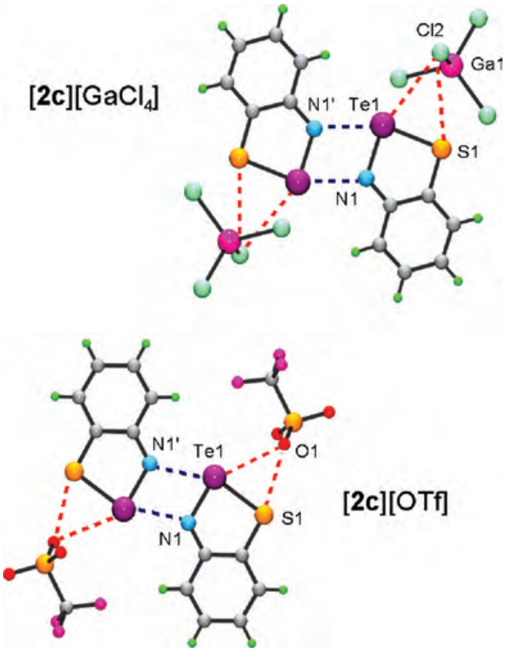

Figure 2. The dimeric ion pair structures of [**2c**][GaCl$_4$] and [**2c**][OTf], with atom numbering. Carbon atom numbering follows Figure 1.

planar 12-electron AX_4E_2 coordination environment. In the case of the $TeCl_5^-$ salt, the anions are also associated by bridging chlorines, to form edge-sharing octahedral $[Te_2Cl_{10}]^{2-}$dianions, and the crystal structure consists of ribbons of alternating $[\mathbf{2c}]_2^{2+}$ dications and $[Te_2Cl_{10}]^{2-}$ anions, as shown in Figure 3. The terminal and bridging Te−Cl bonds within the $[Te_2Cl_{10}]^{2-}$ anions are expectedly in accord with those reported previously for various other salts containing this species.[22,23]

In contrast to the dimeric nature of the simple [**2c**][X] salts, the structure of the $GaCl_3$ complex [**2c**][GaCl$_3$][GaCl$_4$] consists of monomeric cations [**2c**][GaCl$_3$]$^+$ (Figure 4), weakly ion paired via contacts Te1−Cl2′ (3.1633(8) Å) and S1−Cl2′ (3.3019(13) Å) with neighboring $GaCl_4^-$ anions. The [**2c**][GaCl$_3$]$^+$ cation represents a rare example of a positively charged heterocycle serving as a donor to a Lewis

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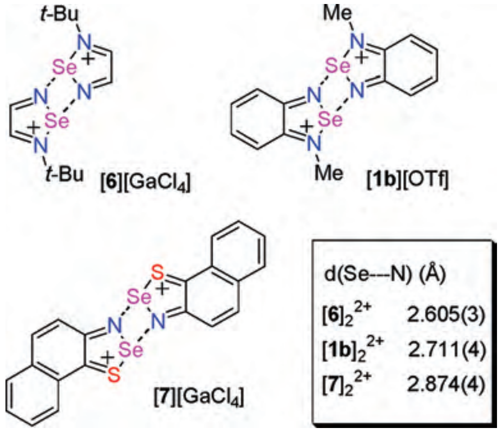
(23) (a) Krebs, B.; Büschner, K. *Z. Anorg. Allg. Chem.* **1980**, *463*, 56. (b) Hauge, S.; Marøy, K. *Acta Chem. Scand.* **1998**, *52*, 445. (c) Hauge, S.; Janickis, V.; Marøy, K. *Acta Chem. Scand.* **1999**, *53*, 992. (d) James, M. A.; Knop, O.; Cameron, T. S. *Can. J. Chem.* **1992**, *70*, 1795. (e) Hauge, S.; Marøy, K. *Acta Chem. Scand.* **1996**, *50*, 1095. (f) Krebs, B.; Paulat, V. *Z. Naturforsch.* **1979**, *34B*, 900. (g) Beck, J.; Hormel, A.; Koch, M. *Eur. J. Inorg. Chem.* **2002**, 2271.

Chart 2



acid.[24] In spite of the overall positive charge on the cation, the nitrogen atom in the cation prefers to coordinate to $GaCl_3$ rather than to develop a 4-center dimer with another cation. Comparison of the C−N and N−Te bond lengths in the dimerized and $GaCl_3$-complexed cations (Table 2) reveal only small differences in the C−N and N−Te distances, suggesting little change in the electronic structure of the ring.

As illustrated in Figure 5, all three cations [**2a**,**b**,**c**]$^+$ show similar trends in the C−C bonds within the benzene ring. The variations, which are well replicated by DFT calculations using the B3LYP hybrid functional, with 6-31G(d,p) basis sets for C, H, N and S, and SDB-cc-pVTZ effective core potential basis sets for Se and Te, suggest the importance of the quinoid valence bond contributor shown in Chart 3.

Redox Chemistry. Our main objective in preparing the heavier members of the series of benzothiachalcazolylium cations [**2a**,**b**,**c**]$^+$ was to probe the possibility of generating radical species by one-electron reduction. As a starting point we carried out DFT calculations to model the spin distributions and ion energetics of the putative radicals. The results are summarized in Figure 6, which shows the calculated B3LYP/6-31G(d,p)/SDB-cc-pVTZ spin densities for the

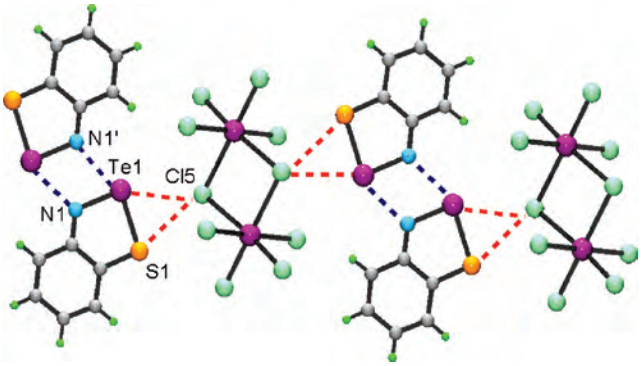


Figure 3. The extended ion pair structure of [**2c**][$TeCl_5$], with atom numbering. Carbon atom numbering follows Figure 1.

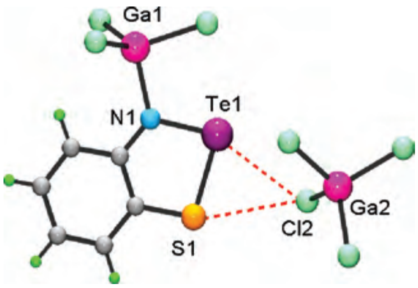


Figure 4. Structure of the monomeric Lewis acid adduct [**2c**]-[$GaCl_3$][$GaCl_4$], with atom numbering. Carbon atom numbering follows Figure 1.

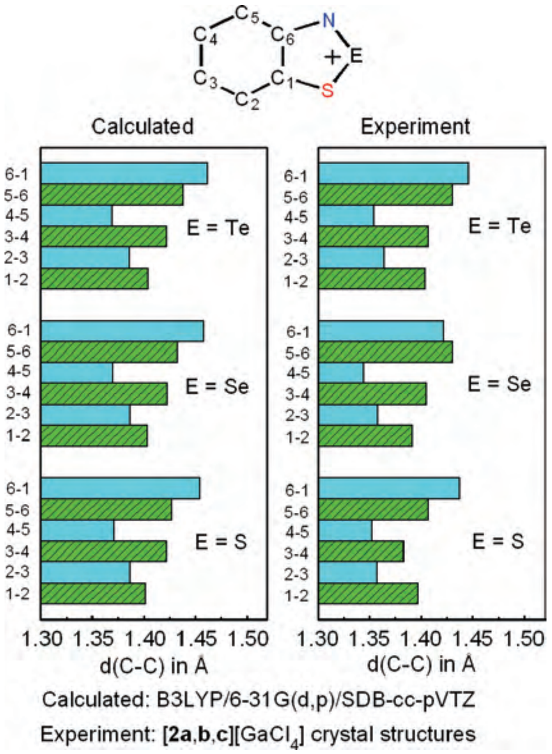
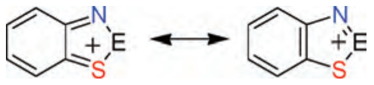


Figure 5. Calculated and experimental C−C distances in [**2a**,**b**,**c**]$^+$ cations.

Chart 3



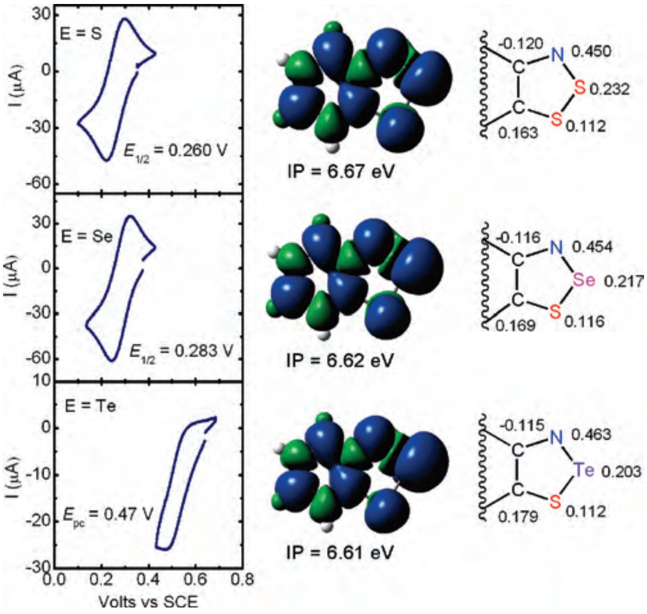


Figure 6. Computed spin distributions for **2a**,**b**,**c** and CV scans for [**2a**,**b**,**c**][$GaCl_4$] in MeCN.

putative radicals **2a**,**b**,**c**. As may be seen the transition from S to Se to Te induces very little change in spin distribution within the heterocycle and, consistently, the computed adiabatic ionization energies for the three radicals are virtually identical.[25]

Also shown in Figure 6 are the results of cyclic voltammetric (CV) analysis of solutions of [**2a**,**b**,**c**][$GaCl_4$] in MeCN. As expected, the S- and Se-based rings show a clear, reversible +1/0 reduction wave at approximately the same $E_{1/2}$ values. In addition both compounds display a second, but irreversible 0/−1 wave with E_{pc} value of −0.96 V (E = S) and −0.90 V (E = Se) versus SCE. The CV behavior of [**2c**][$GaCl_4$] is less straightforward, indeed a reversible wave cannot be obtained for the +1/0 couple, even with fast cycling times and narrow sweep ranges.[26] At best a profile of the type illustrated in Figure 6 is obtained, with a barely discernible cathodic peak with E_{pc} near 0.47 V. Clearly this potential is well removed (more anodic) from the range observed for the reduction of [**2a**,**b**]$^+$, although the difference is not as great as that seen between $E_{1/2}{}^{0/+1}$ couples for [**1a**,**b**]$^+$ and [**1c**]$^+$.

In accord with the electrochemical results, chemical reduction of the chloride salts of [**2a**,**b**][Cl] with triphenylantimony in CH_2Cl_2 affords solutions that show a strong and persistent EPR signal which can be assigned to the respective radicals **2a**,**b**.[27] As illustrated in Figure 7, the X-band EPR spectra of the two radicals are similar, although that of **2b** is broadened by spin−orbit coupling effects from selenium and a consequent anisotropy in the *g*-value.[28] The observed fine structure is dominated by a triplet created by a large hyperfine coupling to the ^{14}N nucleus; this is split into a more complex pattern by virtue of smaller coupling to the four ^1H nuclei on the benzene periphery. The relevant coupling constants a_N and a_H have been extracted by spectral simulation and assignments confirmed by comparison with computed values obtained from DFT calculations (Figure 7).

Attempts to observe an EPR signal for the tellurium based radical **2c** using the same in situ reduction methods described were unsuccessful. However, preparative scale reduction of salts of [**2c**]$^+$ was, however, a relatively clean and reproducible process.[29] For example, reaction of a solution of [**2c**][OTf] in MeCN with dimethylferrocene afforded a metallic gray, microcrystalline powder with an elemental (C, H, N) composition near that expected for the formulation **2c**. The material was not, however, EPR active and, despite repeated attempts, crystals of sufficient size and quality for single crystal X-ray analysis could not be obtained.[30]

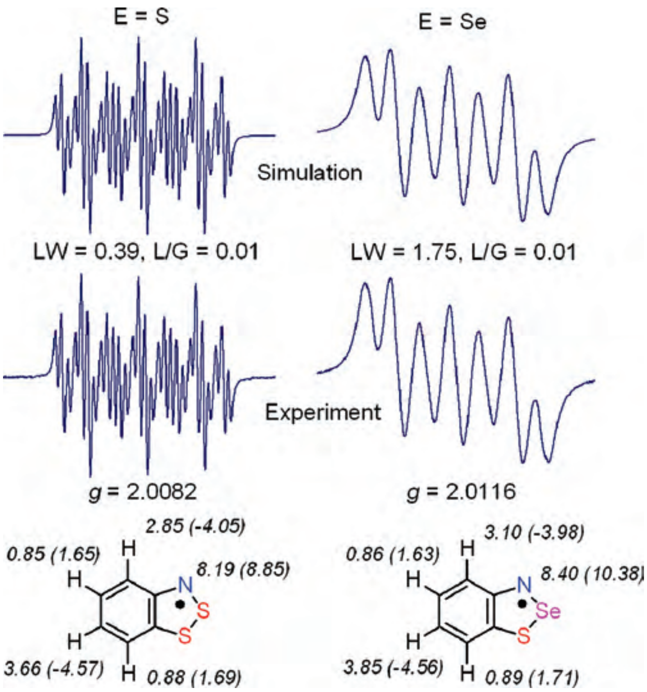


Figure 7. EPR spectra of **2a**,**b**; SW = 40 G. Experimentally derived (by simulation) and calculated (in parentheses) coupling constants (in G) are shown below.

Energetics of Cation Association. The results of structural characterization of several salts of the Te-based cation [**2c**]$^+$ confirm the apparently inevitable tendency of this material to self-associate in the solid state to form centrosymmetric dimers linked via short intermolecular Te−N linkages.[8] This mode of association has often been observed in cyclic and acyclic Te−N compounds[6] and, to a lesser extent, in Se−N compounds.[8,14,17] In the case of chalcodiazoles, where two Te−N linkages are potentially available for intermolecular association, polymeric structures can be generated. Vargas-Baca and co-workers have examined the energetics of association of these heterocycles, and have provided an elegant evaluation of the electronic reasons for the increasing strength of association along the series E = S, Se, Te.[31]

The three cations [**2a**,**b**,**c**]$^+$ reported here constitute the second fully characterized family of heterocyclic chalcogen-

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(24) (a) Sava, X.; Melaimi, M.; Mézailles, N.; Ricard, L.; Mathey, F.; Le Floch, P. *New J. Chem.* **2002**, *26*, 1378. (b) Burford, N.; Losier, P.; Sereda, S. V.; Cameron, T. S.; Wu, G. *J. Am. Chem. Soc.* **1994**, *117*, 6474. (c) Burford, N.; Cameron, T. S.; LeBlanc, D. J.; Losier, P.; Sereda, S.; Wu, G. *Organometallics* **1997**, *16*, 4712. (d) Ritter, S.; Hübener, R.; Abram, U. *J. Chem. Soc., Chem. Commun.* **1995**, 2047.

(25) The spin distributions and ionization energies of 1,2,3-dithiazolyls, including **2a**, have been studied in some detail. See, for example,(a) Kaszynski, P *J. Phys. Chem. A* **2001**, *105*, 7626. (b) Kaszynski, P. *J. Phys. Chem. A* **2001**, *105*, 7615. (c) Cordes, A. W.; Mingie, J. R.; Oakley, R. T.; Reed, R. W.; Zhang, H. *Can. J. Chem.* **2001**, *79*, 1352.

(26) In spite of its low solubility, we have examined the electrochemical behavior of [**2c**][$GaCl_4$] in DCE, in which cation dimerization should be less favorable. The results were very similar to those reported here for MeCN.

(27) Despite many attempts, with different solvents and reducing agents, we have not been able to isolate **2a** or **2b**. Similar difficulties with other monofunctional 1,2,3-dithiazolyls, and their selenium analogues, have been encountered before, although the naphthalene version of **2a** has been structurally characterized (see ref 14).

(28) (a) Bagryanskaya, I. Y.; Gatilov, Y. V.; Gritsan, N. P.; Ikorskii, V. N.; Irtegova, I. G.; Lonchakov, A. V.; Lork, E.; Mews, R.; Ovcharenko, V. I.; Semenov, N. A.; Vasilieva, N. V.; Zibarev, A. V. *Eur. J. Inorg. Chem.* **2007**, 4751. (b) Bestari, K.; Ferguson, G.; Gallagher, J. F.; Oakley, R. T. *Inorg. Chem.* **1992**, *31*, 442. (c) Bestari, K.; Cordes, A. W.; Oakley, R. T.; Young, K. M. *J. Am. Chem. Soc.* **1990**, *112*, 2249.

(29) Electroreduction of [**2c**][$GaCl_4$] affords a black microcrystalline deposit on the electrode. This material is, we presume, the same as that generated by chemical reduction.

(30) The product obtained from the reduction of [**2c**]$^+$ is remarkably robust (air stable). Its infrared spectrum is strong, reproducible and not that of elemental tellurium; it also provided a good powder X-ray diffraction pattern. While we were unable to index this pattern, it was certainly not that of elemental tellurium.

(31) Cozzolino, A. F.; Vargas-Baca, I.; Mansour, S.; Mahmoudkhani, A. H. *J. Am. Chem. Soc.* **2005**, *127*, 3184.

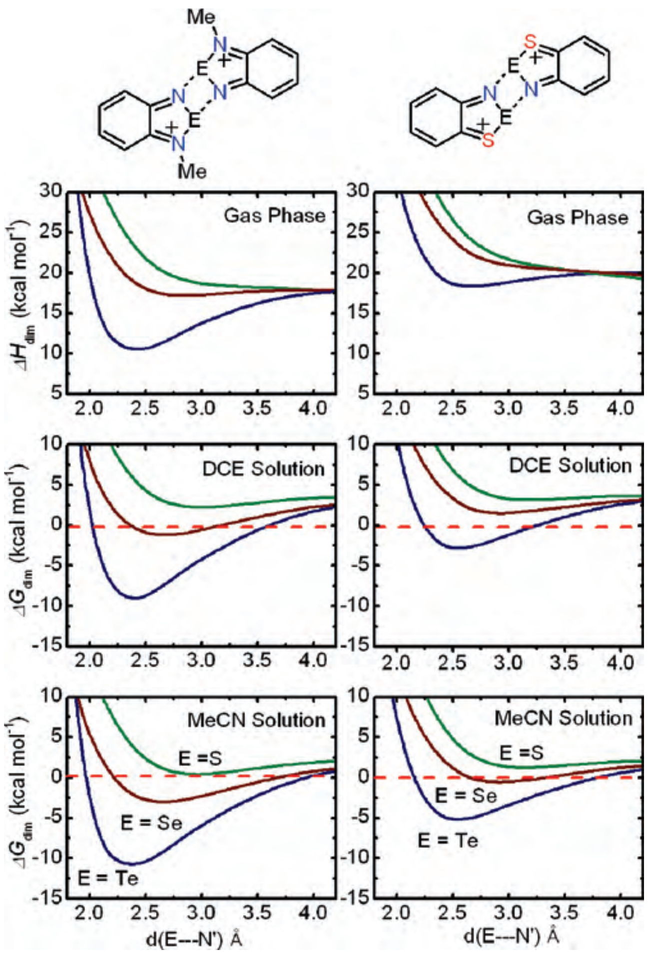
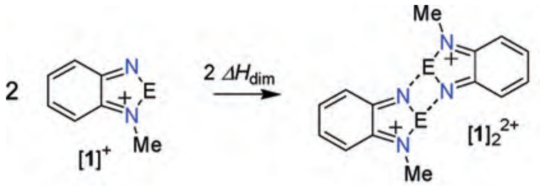
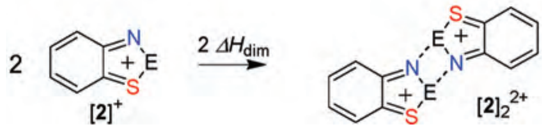


Figure 8. Gas phase ΔH_{dim} and PCM ΔG_{dim} of [**1a**,**b**,**c**]$^+$ (left) and [**2a**,**b**,**c**]$^+$ (right) in MeCN and DCE, plotted as a function of d(E−N′).

nitrogen cations. Taken together with our earlier work on [**1a**,**b**,**c**]$^+$, the results provide an opportunity to probe the strength of intermolecular interactions as a function of ring system and heteroatom. In order to interpret the observed trends, and to provide a quantitative estimate of the energies involved, we have carried out a series of DFT calculations at the B3LYP/6-31G(d,p)/SDB-cc-pVTZ level on both families of cations and their respective dimers. The results are illustrated in Figure 8, which shows plots of the gas phase enthalpy change ΔH_{dim} for the association of the two cations [**1**]$^+$ and [**2**]$^+$ as a function of the interdimer separation d(E−N′) (eqs 1 and 2).



Eqn 1



Eqn 2

As a result of the electrostatic repulsion between the cations, ΔH_{dim} is predicted to be endothermic for both families, regardless of the nature of the chalcogen. The same effect, that is, endothermic heats of association of Group 16 cations, has been observed elsewhere, for example, in the reaction 2 $[SI_2]^+ \rightarrow [S_2I_4]^{2+}$.[32] In the present systems there is a pronounced local minimum for the tellurium based rings [**1c**]$^+$ at 2.389 Å and for [**2c**]$^+$ at 2.668 Å, the former being substantially deeper. There is also a shallow local minimum in [**1b**]$^+$ at 2.811 Å which is completely washed out for [**2b**]$^+$. In neither case does the sulfur-based variant exhibit a minimum. While correlation of the trends in the gas phase local minima with the solid state structures can only be considered as qualitative, it is satisfying to note that the intermolecular Te−N′ contacts in salts of [**1c**]$_2^{2+}$ and [**2c**]$_2^{2+}$ are close to those predicted by the DFT calculations. Similarly, the weaker association of the cation in [**1b**][OTf] (with d(Se−N′) = 2.711(4) Å) and the absence of dimerization in [**2b**][GaCl$_4$] are both consistent with the theoretical predictions.

Of equal if not greater importance to the rationalization of the solid state results is the potential for DFT methods to aid in the assessment of the extent of cation association in solution. The gallate and triflate salts of [**1a**,**b**,**c**]$^+$ and [**2a**,**b**,**c**]$^+$, for example, are sparingly soluble in DCE and liquid SO$_2$, and as a result more polar solvents such as MeCN (and DMSO) were preferred for physical measurements (NMR spectroscopy) as well as electrochemical and bulk chemical reductions. In order to probe the extent of association of [**1a**,**b**,**c**]$^+$ and [**2a**,**b**,**c**]$^+$ in solution, we employed the polarized continuum model (PCM)[33] to assess the effects of the solvent dielectric (ε) on the stability of the dimeric dications relative to the separated monomeric cations. The method, which assesses the interaction of the solvent, represented by a dielectric continuum, has been applied to the study of inorganic and organic ions, including sulfenium cations,[34] in a wide range of solvents.

In the present work we have examined the effects of two solvents, DCE (ε = 10.36) and MeCN (ε = 36.64), and carried out single point calculations of the total free energy of the solvated cations and dications using geometries obtained from the gas phase optimizations. The resulting changes in free energy of dimerization ΔG_{dim} as a function of internuclear separation are shown in Figure 8. As expected, the incorporation of solvation stabilizes the dications by mollifying the repulsive electrostatic interaction between the two cations. As the dielectric constant increases, that is between DCE and MeCN, so too does the stabilization of the dication, to the extent that the free energy minima in MeCN for the tellurium-based dication [**2c**]$^+$ (−5.2 kcal mol^{-1}) and [**1c**]$^+$ (−11.1 kcal mol^{-1}) suggest that dimeric

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(32) (a) Brownridge, S.; Crawford, M.-J.; Du, H.; Harcourt, R. D.; Knapp, C.; Laitinen, R. S.; Passmore, J.; Rautiainen, J. M.; Suontamo, R. J.; Valkonen, J. *Inorg. Chem.* **2007**, *46*, 681. (b) Tuononen, H. M.; Suontamo, R.; Valkonen, J.; Laitinen, R. S. *J. Phys. Chem. A* **2004**, *108*, 5670.

(33) (a) Tomasi, J.; Persico, M. *Chem. Rev.* **1994**, *94*, 2027. (b) Cossi, M.; Barone, V.; Cammi, R.; Tomasi, J. *Chem. Phys. Lett.* **1996**, *255*, 327. (c) Menucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *106*, 5151. (d) Barone, V.; Cossi, M.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3210.

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structure $[\mathbf{2c}]_2^{2+}$ and, more particularly, $[\mathbf{1c}]_2^{2+}$represent the most likely formulations for these species in polar solvents.

Summary and Conclusions

The condensation of persilylated 2-aminobenzenethiol with ECl_4 (E = Se, Te) provides a simple and effective route to heavy atom thiachalcazolylium cations $[\mathbf{2}]^+$. The tendency for salts of the tellurium based cation $[\mathbf{2c}]^+$ to crystallize as centrosymmetric dimers parallels that seen for the related *N*-methyl chalcodiazolylium cation $[\mathbf{1c}]^+$. In support of crystallographic data the results of DFT calculations on the two series of cations $[\mathbf{1a},\mathbf{b},\mathbf{c}]^+$ and $[\mathbf{2a},\mathbf{b},\mathbf{c}]^+$ indicate that association is generically stronger for the former, and that within each series the strength of the intermolecular E−N′ interaction increases with E = S < Se < Te. The weaker association of $[\mathbf{2c}]^+$ (relative to $[\mathbf{1c}]^+$) has allowed the isolation of a monomeric complex $[\mathbf{2c}][GaCl_3][GaCl_4]$, in which the nitrogen atom of the heterocycle is coordinated to $GaCl_3$. In contrast to the behavior of the light atom cations $[\mathbf{1a},\mathbf{b}]^+$and $[\mathbf{2a},\mathbf{b}]^+$, electrochemical reduction of salts of $[\mathbf{1c}]^+$ and $[\mathbf{2c}]^+$ are strongly irreversible, and attempts to observe the putative radical **2c** have been unsuccessful. Chemical reduction of [**2c**][OTf] has, however, afforded a diamagnetic material of nominal composition **2c**, although no structural information could be obtained. Attempts to characterize structurally a related derivative are ongoing.

Experimental Section

General Procedures and Starting Materials. All reactions were carried out under an atmosphere of dry nitrogen. The reagents 2-aminobenzenethiol, hexamethyldisilazane, *n*-butyl lithium (1.6 M in hexanes), chlorotrimethylsilane, thionyl chloride, gallium trichloride, silver triflate (trifluoromethanesulfonate) and dimethylferrocene were obtained commercially. All were used as received, save for dimethylferrocene, which was recrystallized from acetonitrile before use. Selenium tetrachloride was prepared by direct chlorination of selenium,[35] and tellurium tetrachloride by the reaction of tellurium dioxide and chlorotrimethylsilane.[36] All solvents were at least the reagent grade: acetonitrile (MeCN), dichloroethane (DCE), and chlorobenzene were dried by distillation over P_2O_5 under a nitrogen atmosphere prior to use. Melting points are uncorrected. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ. Infrared spectra (Nujol mulls, KBr optics) were recorded on a Nicolet Avatar FTIR spectrometer (at 2 cm^{-1} resolution). ^1H, $^{77}Se\{^1H\}$, and ^{125}Te NMR spectra were recorded on a Bruker Avance 300 spectrometer operating at 300.13, 57.318 and 94.918 MHz, respectively. The spectral widths were 4.34, 56.98, and 75.19 kHz, and the pulse widths were 12.0, 9.70 and 6.30 μs. The pulse delay for proton, selenium, and tellurium was 1.0, 2.0 and 2.0 s, respectively. ^1H NMR spectra are referenced to the solvent signal and are reported relative to Me_4Si. The ^{77}Se and ^{125}Te NMR spectra are referenced externally to a D_2O solution of SeO_2 and H_6TeO_6, and the chemical shifts are reported relative to neat Me_2Se and Me_2Te, respectively [$\delta(Me_2Se) = \delta(SeO_2) + 1302.6$; $\delta(Me_2Te) = \delta(H_6TeO_6) + 712$].

Preparation of Trimethylsilanyl(2-trimethylsilanylsulfanylphenyl)amine 4. A neat mixture of **3** (27.0 g, 216 mmol) and hexamethyldisilazane (56 mL, 265 mmol) was gently refluxed for 16 h. The mixture was concentrated in vacuo to leave a yellow oil that was distilled at 89−91 °C/10^{-2} Torr to yield **4** as a colorless oil (51.7 g, 192 mol, 89%). ^1H NMR ($CDCl_3$): δ 7.36 (d, 1H), 7.12 (tr, 1H), 6.81 (d, 1H), 6.64 (tr, 1H), 4.95 (s, 1H), 0.33 (s, 9H), 0.30 (s, 9H).

Preparation of 1,1,1,3,3,3-Hexamethyl-2-(2-trimethylsilanylsulfanylphenyl)disilazane 5. *n*-Butyl lithium (100 mL, 160 mmol) was added dropwise to a solution of **4** (38.2 g, 142 mmol) in diethyl ether (100 mL) at 0 °C. The mixture was stirred at 0 °C for 30 min and then at room temperature for 1 h to give a white suspension. The suspension was cooled back to 0 °C, and chlorotrimethylsilane (23 mL, 181 mmol) was slowly added via a dropping funnel. The mixture was stirred at room temperature overnight. A white precipitate of LiCl was filtered off, and the solvent was flash distilled from the filtrate to leave a pale yellow oil. Vacuum distillation at 123−125 °C/10^{-2} Torr afforded **5** as a colorless oil, yield 42.5 g (124 mmol, 87%). ^1H NMR ($CDCl_3$): δ 7.33 (d, 1H), 6.95 (m, 3H), 0.41 (s, 9H), 0.08 (s, 18 H). Anal. Calcd. for $C_{15}H_{31}NSSi_3$: C, 52.72; H, 9.14; N, 4.10%. Found: C, 52.88; H, 8.91; N, 4.20%.

Preparation of 3H-Benzo[1,2,3]dithiazolylium Chloride [2a][Cl]. A solution of thionyl chloride (1.75 mL, 24.1 mmol) in 10 mL of MeCN was added dropwise to a solution of **3** (1.00 g, 7.99 mmol) in 25 mL of MeCN at 0 °C. The mixture was stirred for 15 min at room temperature, and then refluxed for 1 h. The resulting golden brown precipitate of [**2a**][Cl] was filtered off, washed with 3 × 15 mL of benzene, and dried in vacuo. Yield 1.20 g (6.33 mmol, 79%). IR (cm^{-1}): 3069 (w), 1583 (m), 1514 (m), 1428 (m), 1338 (m), 1306 (m), 1243 (vw), 1187 (vw), 1129 (m), 1010 (m), 989 (m), 955 (s), 947 (s), 870 (w), 817 (vs), 771 (vs), 739 (s, br), 693 (vs), 611 (m), 529 (vw), 493 (w), 487 (w), 454 (m), 441 (m).

Preparation of 3H-Benzo[1,2,3]dithiazolylium Tetrachlorogallate [2a][GaCl₄]. Gallium trichloride (3.00 g, 17.0 mmol) was added to a slurry of [**2a**][Cl] (3.00 g, 15.8 mmol) in 80 mL of MeCN, and the resulting dark green solution was stirred for 1 h and filtered. The solvent was flash distilled to leave a dark green crystalline mass that was recrystallized from chlorobenzene as yellow plates of [**2a**][$GaCl_4$]. Yield 4.00 g (10.9 mmol, 69%); mp. 180−181 °C. Anal. Calcd. for $C_6H_4Cl_4GaNS_2$: C, 19.70; H, 1.10; N, 3.83%. Found: C, 19.91; H, 1.34; N, 4.00%. IR (cm^{-1}): 3083 (m), 1583 (vs), 1517 (s), 1438 (s), 1425 (vs), 1343 (vs), 1319 (vs), 1250 (w), 1239 (vw), 1178 (vw), 1131 (m), 1067 (vw), 1005 (w), 972 (vw), 953 (m), 944 (w), 813 (vs), 769 (vs), 696 (s), 612 (m), 510 (w), 454 (m), 450 (m). The X-ray quality crystals of [**2a**][$GaCl_4$] were obtained by recrystallization from DCE.

Preparation of 3H-Benzo[1,2,3]thiaselenazolylium Chloride [2b][Cl]. A solution of **5** (2.46 g, 7.20 mmol) in 20 mL of MeCN was added slowly to a slurry of $SeCl_4$ (1.50 g, 6.79 mmol) in 60 mL of MeCN at 0 °C. The mixture was stirred for 30 min at room temperature, and then refluxed for 1 h. The resulting dark brown precipitate of [**2b**][Cl] was filtered off, washed with 3 × 10 mL of MeCN, and dried in vacuo. Yield 1.25 g (5.28 mmol, 78%). IR (cm^{-1}): 3057 (vw), 1605 (w), 1583 (s), 1505 (m), 1432 (m), 1420 (s), 1347 (s), 1340 (s), 1308 (s), 1230 (m), 1184 (w), 1167 (vw), 1131 (m), 1068 (vw), 993 (vw), 965 (vw), 879 (w), 771 (vs), 737 (m), 729 (m), 685 (s), 583 (m), 450 (w).

Preparation of 3H-Benzo[1,2,3]thiaselenazolylium Tetrachlorogallate [2b][GaCl₄]. Gallium trichloride (1.00 g, 5.68 mmol) was added to a slurry of [**2b**][Cl] (1.22 g, 5.16 mmol) in 50 mL of MeCN, and the resulting dark red solution was filtered. The solvent was then flash distilled from the filtrate to leave a dark brown crystalline mass that was recrystallized from DCE as orange-brown

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plates of [**2b**][$GaCl_4$]. Yield 1.51 g (3.66 mmol, 71%); mp. 168−170 °C. Anal. Calcd. for $C_6H_4Cl_4GaNSSe$: C, 17.46; H, 0.98; N, 3.39%. Found: C, 17.50; H, 1.16; N, 3.15%. IR (cm^{-1}): 3083 (w), 1586 (s), 1507 (m), 1428 (s), 1424 (vs), 1344 (vs), 1317 (s), 1242 (w), 1232 (vw), 1179 (vw), 1132 (m), 1065 (vw), 1000 (vw), 773 (vs), 750 (m), 745 (m), 685 (m), 582 (m), 448 (w). $^{77}Se\{^1H\}$ NMR (CD_3CN): δ 1560. The X-ray quality crystals of [**2b**][$GaCl_4$] were obtained by recrystallization from chlorobenzene.

Preparation of 3H-Benzo[1,2,3]thiatellurazolylium Chloride [2c][Cl]. A solution of **5** (4.25 g, 12.4 mmol) in 20 mL of DCE was added slowly to a slurry of $TeCl_4$ (3.04 g, 11.3 mmol) in 200 mL of DCE. The mixture was stirred for 10 min at room temperature and then gently refluxed for 1.5 h. The resulting dark black precipitate of [**2c**][Cl] was filtered off, washed with 3 × 15 mL of DCE, and dried in vacuo. Yield 2.64 g (9.26 mmol, 82%). IR (cm^{-1}): 3074 (vw), 3056 (vw), 3031 (vw), 1585 (m), 1568 (w), 1503 (m), 1449 (vs), 1429 (s), 1422 (vs), 1366 (m), 1354 (m), 1293 (s), 1276 (s), 1248 (s), 1240 (w), 1228 (m), 1159 (m), 1129 (s), 1061 (m), 1029 (s), 925 (vw), 894 (vw), 875 (s), 850 (vw), 829 (vw), 767 (s), 735 (m), 721 (s), 682 (vs), 608 (w), 586 (s), 455 (m), 429 (m).

Preparation of 3H-Benzo[1,2,3]thiatellurazolylium Tetrachlorogallate [2c][$GaCl_4$]. Gallium trichloride (0.322 g, 1.83 mmol) was added to a slurry of [**2c**][Cl] (0.474 g, 1.66 mmol) in 10 mL of MeCN, and the resulting red solution was filtered. The solvent was then flash distilled to leave a dark red microcrystalline solid of [**2c**][$GaCl_4$] which was washed with 10 mL of DCE, filtered off and dried in vacuo. Yield 0.616 g (1.34 mmol, 81%); dec >95 °C. Anal. Calcd. for $C_6H_4Cl_4GaNSTe$: C, 15.62; H, 0.87; N, 3.04%. Found: C, 15.49; H, 1.03; N, 2.92%. IR (cm^{-1}): 1583 (m), 1569 (vw), 1559 (w), 1539 (w), 1503 (m), 1428 (sh, m), 1421 (m), 1362 (w), 1346 (m), 1311 (w), 1261 (vw), 1237 (w), 1229 (vw), 1173 (vw), 1139 (w), 1060 (w), 1022 (vw), 994 (vw), 869 (vw), 800 (br, w), 767 (vs), 741 (s), 717 (s), 678 (vs), 577 (m), 458 (w), 445 (w). ^{125}Te NMR (CD_3CN): δ 1427. The X-ray quality crystals of [**2c**][$GaCl_4$] were obtained by recrystallization from DCE.

Preparation of 3H-Benzo[1,2,3]thiatellurazolylium Trifluoromethanesulfonate [2c][OTf]. Silver triflate (0.799 g, 3.11 mmol)) and [**2c**][Cl] (0.877 g, 3.08 mmol) were stirred at gentle reflux in 70 mL of MeCN for 1.5 h to afford a deep red solution and a white AgCl precipitate. The solution was filtered and concentrated to the volume of 10 mL. The red microcrystalline solid of [**2c**][OTf] was filtered off and dried in vacuo. Yield 0.830 g (2.08 mmol, 68%); dec >130 °C. Anal. Calcd. for $C_7H_4F_3NO_3S_2Te$: C, 21.08; H, 1.01; N, 3.51%. Found: C, 21.23; H, 0.83; N, 3.68%. IR (cm^{-1}): 1511 (w), 1295 (s), 1286 (s), 1232 (s), 1219 (s), 1180 (vw), 1151 (m), 1029 (m), 954 (vw), 759 (m), 743 (vw), 684 (m), 637 (m), 575 (w), 519 (w), 514 (w), 451 (vw). ^{125}Te NMR (CD_3CN): δ 1431. The X-ray quality crystals of [**2c**][OTf] were obtained by recrystallization from MeCN.

Formation of 3H-Benzo[1,2,3]thiatellurazolylium Pentachlorotellurate [2c][$TeCl_5$]. A solution of **5** (3.04 g, 8.90 mmol) in 100 mL of MeCN was added slowly to a slurry of $TeCl_4$ (2.00 g, 7.42 mmol) in 200 mL of MeCN at 0 °C. After stirring the reaction mixture for 2 h at room temperature the resulting dark black powder was filtered, washed with 3 × 10 mL of MeCN and dried in vacuo; yield 1.21 g. Gallium trichloride (0.213 g, 1.21 mmol) was then added to a slurry of this dark black powder (0.313 g) in 25 mL of MeCN. The resulting red solution was filtered after 10 min. The solvent was flash distilled to leave a dark red solid which was heated back into 5 mL of MeCN. Cooling of the red solution in freezer overnight afforded dark red X-ray quality crystals of [**2c**][$TeCl_5$] (0.071 g, 0.128 mmol); dec >125 °C. The IR spectrum of [**2c**][$TeCl_5$] matched that of the original precipitate from condensation reaction above. Anal. Calcd. for $C_6H_4Cl_5NSTe_2$: C, 12.99; H, 0.73; N, 2.53%. Found: C, 13.06; H, 0.83; N, 2.49%. IR (cm^{-1}): 3068 (w), 1585 (m), 1501 (s), 1429 (m, sh), 1421 (s), 1366 (m), 1349 (m), 1238 (s), 1172 (m), 1139 (m), 1062 (m), 1021 (vw), 1004 (vw), 960 (vw), 871 (m), 848 (vw), 767 (vs), 741 (s), 716 (s), 681 (vs), 577 (s), 461 (w), 443 (w).

Preparation of the Gallium Trichloride Complex of 3H-Benzo[1,2,3]thiatellurazolylium Tetrachlorogallate [2c][$GaCl_3$][$GaCl_4$]. Gallium trichloride (0.434 g, 2.46 mmol) was added to a slurry of [**2c**][Cl] (0.335 g, 1.17 mmol) in 15 mL of DCE. The solution was stirred at room temperature for 15 min, and the red microcrystalline solid of [**2c**][$GaCl_3$][$GaCl_4$] obtained by *n*-hexane (30 mL) precipitation was filtered and dried in vacuo. Yield 0.570 g (0.894 mmol, 76%). Anal. Calcd. for $C_6H_4Cl_7Ga_2NSTe$: C, 11.31; H, 0.63; N, 2.20%. Found: C, 11.26; H, 0.86; N, 2.09%. IR (cm^{-1}): 1584 (w), 1511 (m), 1423 (m), 1353 (s), 1261 (vw), 1246 (w), 1178 (vw), 1151 (w), 1066 (w), 1018 (w), 879 (w), 770 (m), 762 (vs), 696 (m), 679 (vw), 593 (w), 449 (vw), 425 (m). ^{125}Te NMR: δ (CD_3CN) 1429; δ (DCE) 1337. The X-ray quality crystals of [**2c**][$GaCl_3$][$GaCl_4$] were obtained by recrystallization from liquid SO_2.

Preparation of 3H-Benzo[1,2,3]thiatellurazolyl 2c. Dimethylferrocene (0.161 g, 0.752 mmol) was added to a solution of [**2c**][OTf] (0.300 g, 0.752 mmol) in 15 mL of degassed MeCN. After stirring the reaction mixture for 15 min at room temperature the resulting metallic gray powder of **2c** was filtered off, washed with 2 × 15 mL of MeCN and dried in vacuo. Yield 0.167 g (0.669 mmol, 89%). Anal. Calcd. for C_6H_4NSTe: C, 28.85; H, 1.61; N, 5.61%. Found: C, 27.79; H, 1.76; N, 4.32%. IR (cm^{-1}): 1528 (w), 1434 (s), 1306 (w), 1262 (w), 1232 (m), 1155 (w), 1060 (m), 1023 (m), 737 (s), 709 (w), 636 (vw), 439 (w).

X-Ray Measurements. Diffraction data for compounds [**2a**][$GaCl_4$], [**2b**][$GaCl_4$], [**2c**][$GaCl_4$], [**2c**][OTf], [**2c**][$TeCl_5$] and [**2c**][$GaCl_3$][$GaCl_4$] were collected on a Bruker SMART APEX CCD-based diffractometer at 296 K, 290 or 200 K using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Crystals were mounted onto glass fibers with silicone oil or epoxy. Crystal data and details of the structure determinations are given in Table 1. All structures were solved by direct methods using SHELXL-97[37] and refined by least-squares methods on F^2 using SHELXL-97 incorporated in the SHELXTL[38] suite program. After the full-matrix least-squares refinement of non-hydrogen atoms with anisotropic thermal parameters, the hydrogen atoms were placed in calculated positions in the aromatic ring (C−H = 0.95 Å). In the final refinement the hydrogen atoms were riding with the carbon atom to which they were bonded. The isotropic thermal parameters of the aromatic hydrogen atoms were fixed at 1.2 times to that of the corresponding carbon atom. The scattering factors for the neutral atoms were those incorporated with the programs.

EPR Spectroscopy. The X-band EPR spectra of **2a** and **2b** were recorded at ambient temperature using a Bruker EMX-200 spectrometer. The radicals **2a** and **2b** were conveniently generated by in situ reduction of a slurry of the appropriate chloride salt [**2a**,**b**][Cl] with triphenylantimony in dichloromethane. Hyperfine coupling constants were obtained by spectral simulation using PEST WinSim[39] and Bruker WinEPR Simfonia.[40]

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Cyclic Voltammetry. Cyclic voltammetry was performed using a PINE Bipotentiostat, model AFCClBP1, with scan rates of 100 mV s^{-1} on solutions ($<10^{-3}$ M) of [**2a**,**b**,**c**][$GaCl_4$] in oxygen free MeCN (dried by distillation from P_2O_5) containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate. Potentials were scanned with respect to the quasi-reference electrode in a single-compartment cell fitted with Pt electrodes and referenced to the Fc/Fc^+ couple of ferrocene at 0.38 V vs SCE.[41] The $E_{pa} - E_{pc}$ separation of the reversible couple of $[\mathbf{2a},\mathbf{b}]^+$ was within 10% of that of the Fc/Fc^+ couple.

Theoretical Calculations. Density functional theory calculations were performed with the Gaussian 03 suite of programs,[42] using the B3LYP hybrid density functional with the 6-31G(d,p) basis set for light atoms (H, C, N, S). The relativistic effective core potential basis set SDB-cc-pVTZ was used for selenium and tellurium.[43] The gas phase dimerization enthalpy of the $[\mathbf{2}]^+$ cations was evaluated in terms of the energetic difference between the cations and their respective dications as a function of internuclear separation. Total electronic energies of the gas phase cations M^+ were derived from geometries fully optimized within C_s (planar) symmetry. That these geometries were stationary points was confirmed by frequency calculations. Total electronic energies of the gas phase dications $[\mathbf{2}]_2^{2+}$ were computed using structures optimized within a C_{2h} symmetry constraint, using the two equivalent intermolecular E−N′ distances as the reaction coordinate. The effects of solvation in dichloroethane and acetonitrile were investigated using the polarization continuum solvation model (PCM),[33,44] with atom radii defined by the united simple atom topological (UA0) model. Convergence over the d(E−N′) range of 1.8−6.0 Å required a solvent-specific scaling parameter set at $\alpha = 1.0$ (for E = S) and $\alpha = 1.2$ (for E = Se, Te). Given the size of the dications, no attempt was made to probe structural relaxation in solution; instead, single point calculations were performed using molecular parameters obtained from the gas phase optimizations over a range of intermolecular distances d(E−N′). Gas phase molecular ion energetics, spin densities and hyperfine coupling constants were evaluated using the same method and basis sets noted above. Adiabatic ionization potentials (IP) and electron affinities (EA) were calculated using ΔSCF methods on fully optimized anions, radicals and cations.

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Supporting Information Available: Details of X-ray crystallographic data collection and structure refinement at ambient temperature, tables of atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom positions in CIF format. This information is available free of charge via the Internet at http://pubs.acs.org.

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