

DOI: 10.1002/cphc.200((will be filled in by the editorial staff))

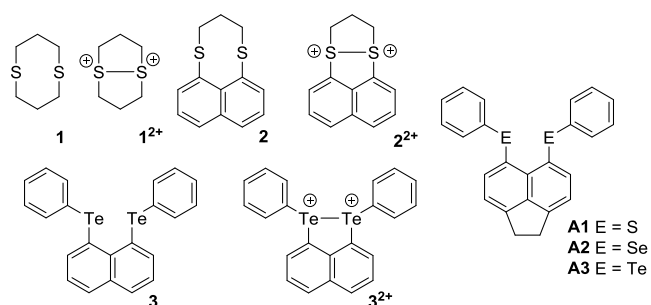
## Electrochemically Informed Synthesis: Oxidation versus Coordination of 5,6-bis(phenylchalcogeno)acenaphthenes

Fergus R. Knight, Rebecca A. M. Randall, Tracey L. Roemmele, René T. Boéré, Bela E. Bode, Luke Crawford, Michael Bühl, Alexandra M. Z. Slawin and J. Derek Woollins[\*]

**This work is dedicated in memory of Dr Nigel Botting, who died after a short battle with cancer in June 2011 aged 48. He is sadly missed by friends, colleagues and students in St Andrews.**

Persistent and stable radicals of the heavier main-group elements are currently attracting considerable attention as functional molecular materials in which the unpaired electron associated with the radical species acts as a charge carrier and/or magnetic coupler, forming non-metallic ferromagnets and electrically conductive main-group compounds.<sup>[1-4]</sup> Overcoming factors which affect radical stability of heavy main group elements is therefore a synthetic challenge, whilst the value of these species for use as modern materials stems from the ability to understand and thus tune their magnetic and electronic properties.<sup>[1-3]</sup>

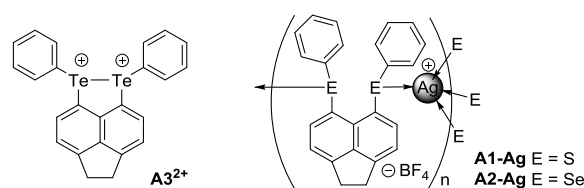
The possibility that an E...E' intramolecular interaction could serve to stabilise chalcogen radical cations and dications was first reported by Musker and Asmus following studies of 1,5-dithiocane **1** (Scheme 1) and related cyclic and acyclic sulfur compounds.<sup>[5,6]</sup> A short time later, Furukawa and coworkers isolated the structure of **1**<sup>2+</sup>, which was the first example of a cyclic dithiocane dication.<sup>[7]</sup> Subsequently they proposed the existence of the Te analogue of **1**<sup>2+</sup> based in particular on Te NMR.<sup>[7]</sup> Glass *et al.* subsequently proposed that the effects reported by Musker and Asmus may be enhanced in a geometrically constrained derivative of 1,5-dithiocane, naphtho[1,8-*b,c*]-1,5-dithiocin **2** (Scheme 1), in which the geometry and rigidity of the naphthalene ring created a greater overlap of the sulfur p type lone pair orbitals, thus increasing the lone-pair lone-pair interaction.<sup>[8]</sup> Oxidation of naphtho[1,8-*b,c*]-1,5-dithiocin **2** was subsequently achieved using D<sub>2</sub>SO<sub>4</sub> as an oxidant, with the stereochemistry of the naphthalene based 1,2-dication **2**<sup>2+</sup> proposed via <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.<sup>[9]</sup> In a further development, Furukawa *et al.* reported a similar oxidation of the non-cyclic bis-tellurium derivative **3**, with a dramatic downfield shift observed in the <sup>125</sup>Te NMR spectrum ( $\delta = 964$  ppm **3**<sup>2+</sup> (D<sub>2</sub>SO<sub>4</sub>), *cf.*  $\delta = 617$  ppm **3** (CDCl<sub>3</sub>)) indicative of a dicationic structure (**3**<sup>2+</sup>, Scheme 1).<sup>[10]</sup> Nonetheless these dication species remain elusive and difficult to isolate with only five known examples having been isolated and crystallographically characterised.<sup>[11]</sup>



**Scheme 1.** *Peri*-substituted chalcogen systems are prime candidates for stabilizing radicals and 1,2-dications.

Nonbonded intramolecular interactions, long known to exist between large heteroatoms in *peri*-substituted species, have been studied in naphthalenes and related acenaphthenes incorporating elements of Groups 15-17.<sup>[12-22]</sup> In a systematic study of corresponding Nap[EPh][E'Ph] and Acenap[EPh][E'Ph] compounds (Nap = naphthalene-1,8-diyl; Acenap = acenaphthene-5,6-diyl; E/E' = S, Se, Te), we found that under the appropriate geometric conditions, repulsion occurring between the heavier chalcogen congeners is counterbalanced by the formation of *quasi*-linear C<sub>Ph</sub>-E...E' three-body fragments, adding an attractive component to the *peri*-interaction in the form of a three-centre, four electron type bond.<sup>[14,18,22]</sup>

We speculated that the unique geometry of these *peri*-substituted systems could provide the stability required for preparing chalcogen radicals and 1,2-dications similar to dications **2**<sup>2+</sup><sup>[9]</sup> and **3**<sup>2+</sup><sup>[10]</sup> via successive one-electron oxidations of the parent compounds. In the present paper we describe the electrochemically informed synthesis of tellurium dication **A3**<sup>2+</sup> (Scheme 2) from the reaction of 5,6-bis(phenyltellurium)acenaphthene **A3** (Scheme 1) with one-electron oxidants silver(I) tetrafluoroborate (AgBF<sub>4</sub>) and silver(I) trifluoromethanesulfonate (AgOTf). Under the same experimental conditions, analogous compounds **A1** and **A2**, bearing the lighter Group 16 congeners (S, Se), favour coordination over oxidation when treated with AgBF<sub>4</sub>, affording two isomorphous three-dimensional (3D) silver(I) supramolecular coordination networks (**A1-Ag**, **A2-Ag**, Scheme 2).



**Scheme 2.** Products from the reaction of Acenap[EPh]<sub>2</sub> compounds **A1-A3** with Ag(I) Salts.

Cyclic voltammograms (CVs) were obtained for **A1-A3** at GC and Pt electrodes (Figure 1, Table 1). In CVs of all three compounds, three oxidation but no reduction processes are evident up to the solvent/electrolyte limits ( $-2.4$  V;  $> +1.8$  V). The CV of **A1**, displays a moderately large return wave for the first oxidation process at  $E_{m1} = 0.62$  V which does not increase with increasing scan rate whilst the second oxidation process with  $E_{p2} = 1.12$  V is irreversible (IRR) at scan rates below  $10$  V s<sup>-1</sup>. At the latter or higher rates, only a minor return wave appears. In contrast, the first oxidation process for compound **A2** with  $E_{m1} = 0.48$  V has a large return wave over all scan rates, whilst the second at  $E_{m2} = 0.76$  V has a moderate return wave

[a] Prof J D Woollins, Prof A.M.Z.Slawin, Prof. M. Bühl, Dr B. E. Bode, Dr F.R. Knight, Ms R.A.M. Randall, Mr L.Crawford. EaSTCHEM School of Chemistry University of St Andrews, St Andrews KY16 9ST Fax: (+) 44 1334 463808 E-mail: jdw3@st-and.ac.uk

[b] Prof R. Boere, Dr T L. Roemmele ((Department)) Dept of Chemistry University of Lethbridge, Canada

Supporting information for this article is available on the WWW under <http://www.chemphyschem.org> or from the author

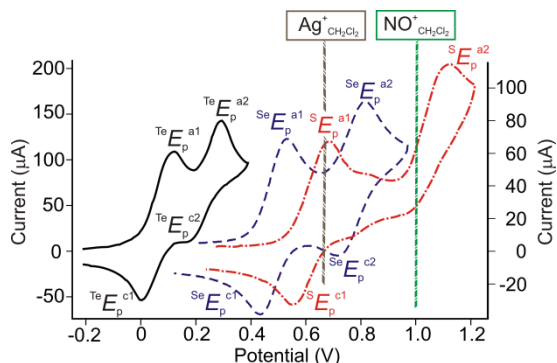
which grows slightly in peak current height with increasing scan rate. For compound **A3**, the closely spaced processes occur at  $E_{m1} = 0.05$  V and  $E_{m2} = 0.21$  V. All processes appear at best *quasi-reversible* (QR) based on the anodic-cathodic peak separations (Table S1) and unequal  $I_a$  and  $I_c$  values, consistent with substantial molecular reorganization accompanying electron transfer (see below). The overlaid CVs in Figure 1 highlight the dramatic chalcogen-dependence of the voltammetric processes; changing S→Se→Te results in both a steep reduction in the onset potential for oxidation and in the spacing of the waves such that  $\Delta E_p$  is only 0.17 V for **A3**. The validity of interpreting  $E^1$  and  $E^2$  as sequential one-electron oxidations is substantiated by peak current heights congruent with equimolar internal reference as well as by the observations of radicals subsequent to  $E^1$ . (For each species, an additional process is observed at substantially higher potentials (Table S1) which are IRR and are not further discussed.)

The CV studies were complemented by DFT (B3LYP) calculations, calling special attention to the conformational preferences of the phenyl substituents as a function of the oxidation state. As the Wiberg bond index (WBI),<sup>[23]</sup> a measure for the covalent character of a bond, increases from the neutral molecules (ca. 0.07-0.14) via the radical cations (0.06-0.21) to the dications (0.18-0.75), the conformational preference changes from an in-plane/perpendicular or trans-orientation of the two phenyl groups to a cis-orientation (see Tables S2-S4 in the Electronic Supporting Information, ESI). For the ditelluride **A3**<sup>2+</sup> such a cis-orientation is indeed found in the solid (see Figure 2 below). The disulfide monocation is unique in that an in-plane conformation of both Ph groups is predicted (BB conformation in Table S3), a minimum that is solely found for this species. The computed trend in the adiabatic first ionisation potentials follows that observed in the  $E^1$  values reasonably well, with a slight decrease on going from **A1** to **A2** (observed 0.13-0.16 V, calculated 0.16 V), and a larger one on going from **A2** to **A3** (observed 0.41-0.42 V, calculated 0.29 V, see dispersion- and solvation- corrected enthalpies in Table S6). The close energies of several geometric isomers adds considerable complexity to this analysis, but it seems certain that reorganization driven by E-E' bonding accompanies oxidation.

**Table 1.** Cyclic Voltammetry data (V) for compounds **A1** – **A3** in CH<sub>2</sub>Cl<sub>2</sub>.<sup>a</sup>

	Electr.	$E_p^{a1}$	$E_p^{c1}$	$E_{m1}^b$	$E_p^{a2}$	$E_p^{c2}$	$E_{m2}^c$	$\Delta E_p^{(a2-a1)^c}$
<b>A1</b>	GC	0.69	0.54	0.62	1.12	— <sup>d</sup>	—	0.43
	Pt	0.66	0.55	0.61	1.09	— <sup>d</sup>	—	0.43
<b>A2</b>	GC	0.53	0.43	0.48	0.81	0.70	0.76	0.28
	Pt	0.53	0.43	0.48	0.81	0.69	0.75	0.28
<b>A3</b>	GC	0.12	-0.01	0.06	0.29	0.15	0.22	0.17
	Pt	0.10	0.00	0.05	0.27	0.15	0.21	0.17

<sup>a</sup> All potentials are reported versus the operative formal potential,  $E^{0'}$  for the  $\text{Fc}^{0/+}$  redox couple, which was used as an internal standard; 0.4 M [<sup>n</sup>Bu<sub>4</sub>N][PF<sub>6</sub>] supporting electrolyte,  $\nu = 0.2$  V s<sup>-1</sup>. <sup>b</sup>  $E_{m1} = [E_p^{a1} + E_p^{c1}]/2 \approx E^{0'}$ . <sup>c</sup>  $E_{m2} = [E_p^{a2} + E_p^{c2}]/2 \approx E^{0'}$ . <sup>d</sup> Separation between first and second processes, in V. <sup>e</sup> A return wave appears at  $\nu = 10$  V s<sup>-1</sup>.

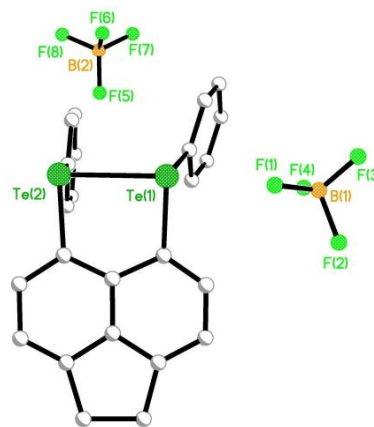


**Figure 1.** Right to left: CVs of (a) 5.4 mM solution of **A1** T = 22.4 °C; (b) 2.7 mM solution of **A2** T = 21.9 °C; (c) 5.5 mM solution of **A3** T =

21.8 °C; current axes: lhs for (a) and (c); rhs for (b). All samples in CH<sub>2</sub>Cl<sub>2</sub> (0.4 M [<sup>n</sup>Bu<sub>4</sub>N][PF<sub>6</sub>]),  $\nu = 0.2$  V s<sup>-1</sup>, on a GC electrode. Vertical markers indicate the formal potentials of chemical oxidants in CH<sub>2</sub>Cl<sub>2</sub>.

In our efforts to access the radicals **A<sup>•+</sup>** and dications **A<sup>2+</sup>** we turned to the well-known tabulation of redox agents by Connelly and Geiger.<sup>[24]</sup> Ag<sup>+</sup> salts with weakly coordinating anions were considered because such anions can greatly stabilize electrophilic cations. Moreover, Ag<sup>+</sup> is more strongly oxidizing (0.65 V vs.  $\text{Fc}^{0/+}$ ; Figure 1) in CH<sub>2</sub>Cl<sub>2</sub> which is an attractive solvent for the acenaphthenes. The thermodynamic relationship between mid-point potentials for oxidant and reductant requires the oxidant to be ~0.12 V more positive to get at least 10:1 product.<sup>[24]</sup> Thus the observation that the reversible potentials for the **A3**<sup>0/+</sup> (0.05 V) and **A3**<sup>+2/+</sup> (0.15 V) processes are both sufficiently more negative than that of the Ag<sup>0/+</sup> couple indicates that reaction of **A3** with Ag<sup>+</sup> salts should permit oxidation of **A3** to the dication **A3**<sup>2+</sup> in this solvent system. We found that treatment of **A3** with two equivalents of AgBF<sub>4</sub> or AgOTf in dichloromethane under an oxygen- and moisture-free nitrogen atmosphere, provided an electrochemically informed route for the chemical synthesis of **A3**<sup>2+</sup> (**A3**<sup>2+</sup>[BF<sub>4</sub>]<sub>2</sub> 74%, **A3**<sup>2+</sup>[OTf]<sub>2</sub> 87%). In each case, a large downfield shift was observed in the <sup>125</sup>Te NMR spectrum compared to the neutral compound **A3** ( $\delta = 585.9$  ppm)<sup>[18]</sup> with single peaks at  $\delta = 931.7$  ppm (**A3**<sup>2+</sup>[BF<sub>4</sub>]<sub>2</sub>) and  $\delta = 964.7$  ppm (**A3**<sup>2+</sup>[OTf]<sub>2</sub>), indicative of dicationic species.<sup>[10,14,20]</sup>

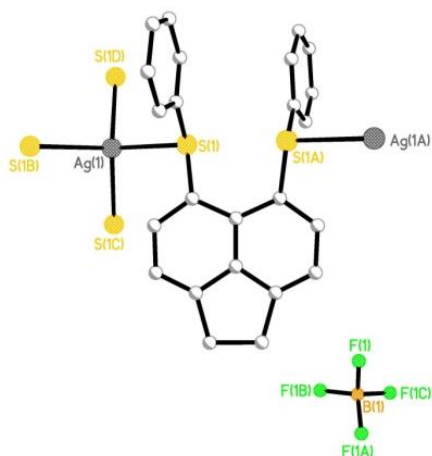
Crystals suitable for X-ray diffraction were obtained by recrystallization from slow diffusion of chloroform into a saturated acetone solution of the respective product at room temperature. Within each molecular structure, the **A3**<sup>2+</sup> acenaphthene fragment adopts an AA-type configuration,<sup>[13,18,25]</sup> aligning both phenyl rings perpendicular (axial) and *cis* to the mean acenaphthene plane (Figure 2). The Te-Te bond distances of 2.8100(19) Å and 2.7960(7) Å are ~1.3 Å shorter than the sum of the van der Waals radii and ~0.6 Å shorter than the neutral species **A3** (3.367(1) Å),<sup>[18]</sup> corresponding to a computed WBI of 0.67 (AAc isomer in Table S3).<sup>[23]</sup> The formation of an attractive Te-Te covalent bond across the *peri-gap* in each **A3**<sup>2+</sup> fragment is accompanied by a natural reduction in molecular distortion which is best highlighted by comparing the in-plane distortion within the bay region. The reduction in splay angle from 18.4° in the neutral and non-bonding compound **A3**<sup>[18]</sup> to 5.3° and 6.0° in the two **A3**<sup>2+</sup> dications, represents the bay region angles becoming more acute as the exocyclic C-Te bonds come together as a result of bond formation. The Te(1)...F(1) distance is 2.771(14) Å and the Te(2)-Te(1)...F(1) angle is 175.4(3)°.



**Figure 2.** The molecular structure of  $[\{\text{Acenap}(\text{TePh})_2\}^{2+}(\text{BF}_4)_2]$  **A3**<sup>2+</sup>[BF<sub>4</sub>]<sub>2</sub> (H atoms omitted for clarity). The structure of **A3**<sup>2+</sup>[OTf]<sub>2</sub> is omitted here but can be found in the ESI.

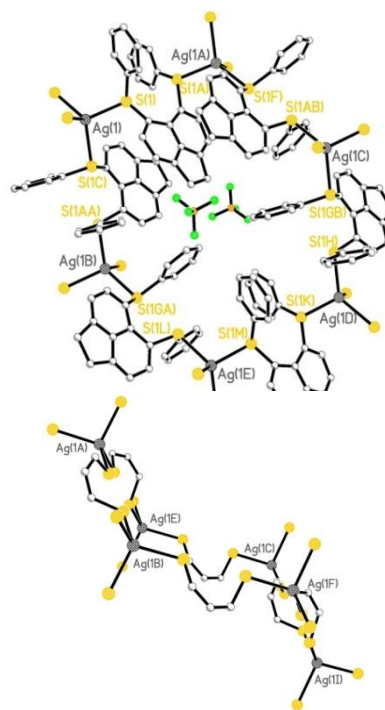
The applicability of Ag<sup>+</sup> salts for oxidation of **A1** and **A2** is more nuanced than is the case for **A3**. Certainly,  $E_{m1}$  for **A2** is sufficiently negative to predict at least a ten-fold excess of product (requires  $E_{m1} \leq +0.53$  V in CH<sub>2</sub>Cl<sub>2</sub>); more importantly, however, double oxidation ought not to occur even with an excess of reagent and we hoped therefore to be able to isolate salts of the radical cation **A2**<sup>•+</sup>. For **A1**,

on the other hand,  $\text{Ag}^+$  salts are not expected to have sufficient strength even in  $\text{CH}_2\text{Cl}_2$  to affect oxidation. Indeed, under similar reaction conditions to those employed for the oxidation of **A3** to **A3<sup>2+</sup>**, 5,6-bis(phenylsulfanyl)acenaphthene **A1** reacted with a single equivalent of silver tetrafluoroborate [ $\text{AgBF}_4$ ] in dichloromethane to afford a three-dimensional (3D) silver(I) supramolecular coordination network [ $\text{Ag}(\text{BF}_4)\{\text{Acenap}(\text{SPh})_2\}_2\}_n$  **A1-Ag** (Figure 3). Interestingly, treatment of the selenium derivative, 5,6-bis(phenylselenyl)acenaphthene **A2**, with  $\text{AgBF}_4$  in dichloromethane afforded the isomorphous selenium analogue of network **A1-Ag**, [ $\text{Ag}(\text{BF}_4)\{\text{Acenap}(\text{SePh})_2\}_2\}_n$  **A2-Ag** and not the cation radical **A2<sup>•+</sup>**. Just as more coordinating solvents reduce the oxidative strength of  $\text{Ag}^+$ , we propose that coordination to Se also suppresses the desired redox reaction; as the results of this study clearly indicate, **A1** and **A2** are indeed excellent ligands for silver(I).



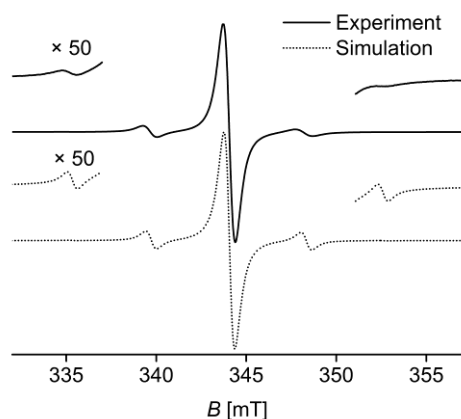
**Figure 3.** The  $\mu_2$ -bridging mode of ligand **A1** in network **A1-Ag** showing bis-monodentate coordination to independent silver(I) ions (H atoms omitted for clarity). The structure of **A2-Ag** (adopting the same configuration) is omitted here but can be found in the ESI.

The two coordination polymers, adopting the same structural architecture, are constructed from a charged continuous  $\text{Ag}(\text{L})_2$  framework ( $\text{L} = \text{A1/A2}$ ). Within each extended network, the bis-chalcogen ligand (**A1/A2**) acts as a  $\mu^2$ - $\eta^2$ -bridging unit, coordinating through both chalcogen donor atoms to link two independent silver(I) ions (bis-monodentate; Figure 3).<sup>[26]</sup> Each silver(I) centre is thus tetrahedrally coordinated to four S/Se atoms of four independent ligands, and by association connected to four adjacent silver(I) ions. Six  $\text{Ag-L}$  units ( $\text{L} = \text{A1/A2}$ ) combine to form 36-membered “hexagonal” macrometallacyclic rings in which silver ions occupy the six corners of the hexagon and  $\mu^2$ - $\eta^2$ -bridging ligands act as the six edges (Figure 4). The macrocycles adopt chair configurations and the  $\text{Ag}\cdots\text{Ag}$  sides are of equal length as a consequence of the symmetry [**A1-Ag** 8.713(1) Å; **A2-Ag** 8.807(1) Å]. Further details are provided in the ESI.



**Figure 4.** Upper: The hexagonal macrometallacyclic ring of **A1-Ag** formed from six  $\text{Ag-A3}$  units (H atoms omitted for clarity); Lower: The chair configuration of the macrocycle (phenyl and acenaphthene rings omitted for clarity) Similar images for **A2-Ag** are omitted here but can be found in the ESI.

Silver is not a suitable oxidant for the S and Se systems since coordination of  $\text{Ag}^+$  further reduces its strength as an oxidant. However, the  $\text{NO}^{0/+}$  couple (1.00 V in dichloromethane)<sup>[24]</sup> is sufficiently more positive than the values of  $E_{m1}$  for the **A2<sup>0/+</sup>** (0.48 V), and **A1<sup>0/+</sup>** (0.62 V) processes, indicating reaction of  $\text{NO}^+$  salts with **A2** and **A1** should permit oxidation to cation radicals **A2<sup>•+</sup>** and **A1<sup>•+</sup>**. Moreover, this reactant also does not exceed  $E_{m2}$  for **A2** enough to convert more than 99% **A2<sup>•+</sup>** to **A2<sup>2+</sup>**<sup>[23]</sup> and 1% radical is more than enough for detection of the radical by EPR spectroscopy. Indeed treatment of **A2** with  $\text{NOBF}_4$  (1:1 ratio in  $\text{CH}_2\text{Cl}_2$  under similar reaction conditions employed for the silver salts), produced an immediate colour change upon addition of the nitrosonium salt, encountering an intense ink blue solution which gradually faded over a few hours. The corresponding reaction of sulfur derivative **A1** with  $\text{NOBF}_4$  gave a similar colour transformation, instantly turning the reaction mixture a vibrant red. Investigations of these intensely coloured intermediates by EPR showed the presence of radical species. For completeness the reaction of tellurium analogue **A3** with  $\text{NOBF}_4$  was also investigated. As expected from the electrochemistry data ( $E_{m2} = 0.21$ – $0.22$  V), no intense colour change was observed upon the addition of  $\text{NO}^+$  suggesting a radical species was not present. Instead oxidation to the dication **A3<sup>2+</sup>** [ $\text{BF}_4$ ]<sub>2</sub> was observed in near quantitative yield.



**Figure 6.** EPR of  $A2^{+\bullet}$ . Room temperature X-band cw-EPR spectrum of the reaction of  $A2$  with  $NOBF_4$  in  $CH_2Cl_2$ . The simulation is based on two  $^{77}Se$  nuclei in natural abundance.

The room temperature continuous wave EPR of  $A2^{+\bullet}$  exhibits a strong central line at  $g = 2.0290(5)$  with  $^{77}Se$  satellites split by an isotropic hyperfine splitting of  $245(3)$  MHz. Close inspection reveals a second set of satellites which is attributed to 0.6% of the radical being delocalised over two  $^{77}Se$  nuclei. The spectrum could be satisfactorily simulated<sup>[27]</sup> assuming binuclear selenium radical in natural abundance leading to the respective probabilities of observing none, one and two  $^{77}Se$  nuclei of 85.4, 14.0 and 0.6%. Proton hyperfine couplings are not resolved due to the large peak-to-peak line width of 0.6 mT for the central line (typical for  $^{77}Se$  and usually attributed to spin-orbit coupling effects). Preliminary spectra of  $A1^{+\bullet}$  (Figure S4) show a complicated pattern of several sets of partially resolved proton hyperfine couplings. The quantification of the  $A1^{+\bullet}$  is an on-going EPR/DFT effort and will be reported in due course.

## Experimental Section

Unless otherwise stated, all reactions were carried out under an oxygen free nitrogen atmosphere using pre-dried solvents and standard Schlenk techniques, subsequent chromatographic and work up procedures were performed in air.  $^1H$  (270 MHz),  $^{13}C$  (67.9 MHz),  $a^{77}Se$ - $\{^1H\}$  (51.4 MHz referenced to external  $Me_2Se$ )  $^{125}Te$  (85.2 MHz referenced to external  $Me_2Te$ , with a secondary reference to  $(PhTe)_2$ ;  $\delta(Te) = 428$  ppm) NMR spectra were recorded at 25 °C (unless stated otherwise) on a JEOL GSX 270. IR spectra were recorded as KBr pellets in the range of 4000-250  $cm^{-1}$  on a Perkin-Elmer 2000 FTIR/Raman spectrometer. X-ray crystal data for compounds  $A2-Ag$  and  $A3^{2+}[BF_4]_2$  were collected using the STANDARD automated system,<sup>[28]</sup> for  $A3^{2+}[OTf]_2$  using a Rigaku Mercury and for  $A1-Ag$  using a Rigaku SCX-Mini. Intensity data were collected using  $\omega$  steps accumulating area detector images spanning at least a hemisphere of reciprocal space. All data were corrected for Lorentz polarization effects. Absorption effects were corrected on the basis of multiple equivalent reflections or by semi-empirical methods. Structures were solved by direct methods and refined by full-matrix least-squares against  $F^2$  by using the program SHELXTL. Hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealized geometries. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) or from the Cambridge Crystallographic Data centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax (+44) 1223-336-033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).  $A3^{2+}[BF_4]_2$  938655,  $A3^{2+}[OTf]_2$  938656,  $A1-Ag$  873008,  $A2-Ag$  873013.

$A3^{2+}[BF_4]_2$ ,  $A3^{2+}[OTf]_2$ ,  $A1-Ag$  and  $A2-Ag$  were prepared by a similar method as described below: to a solution of the respective oxidant ( $AgBF_4/AgOTf/NOBF_4$ ) in dichloromethane was added one molar equivalent of the chalcogen donor ligand ( $A1-A3$ ) in one batch at -30 °C. The reaction mixture was stirred at this temperature for 3 h and then at room temperature for a further 12 h. The solvent was removed

*in vacuo*. The crude product was washed with diethyl ether and the precipitate which formed was collected by filtration. An analytically pure sample of the respective product was obtained by recrystallisation.

**DFT computations** were performed at the B3LYP/6-31+G\* level, using a polarized Binning-Curtiss basis on Se and the relativistic Stuttgart-Dresden pseudopotential on Te. Full computational and experimental details and characterisation can be found in the ESI.

In conclusion this work has demonstrated the utility of electrochemical studies in designing synthetic strategies. We have isolated and crystallographically characterised silver network complexes of sulfur and selenium systems whilst also isolating a dicationic Te-Te bonded species under similar reaction conditions. Using a stronger oxidising agent enabled the observation by EPR of the one electron radical cations derived from the sulfur and selenium acenaphthalenes.

## Acknowledgements

((Acknowledgements Text))

**Keywords** radical · 1,2-dication · chalcogen · EPR · DFT · X-ray crystallography

- [1] P. P. Power, *Chem. Rev.* **2003**, *103*, 789-809. R. T. Boeré, *Electron Paramagn. Reson.* **2013**, *23*, 22-57. R. G. Hicks, *Stable Radicals: Fundamental and Applied Aspects of Odd-Electron Compounds*, John Wiley & Sons.: Chichester, U.K., **2010**.
- [2] A. A. Leitch, K. Lakin, S. M. Winter, L. E. Downie, H. Tsuruda, J. S. Tse, M. Mito, S. Desgreniers, P. A. Dube, S. Zhang, Q. Liu, C. Jin, Y. Ohishi, R. T. Oakley, *J. Am. Chem. Soc.* **2011**, *133*, 6051-6060. S. M. Winter, S. Datta, S. Hill, R. T. Oakley, *J. Am. Chem. Soc.* **2011**, *133*, 8126-8129. A. Mailman, S. M. Winter, X. Yu, C. M. Robertson, W. Yong, J. S. Tse, R. A. Secco, Z. Liu, P. A. Dube, J. A. K. Howard, R. T. Oakley, *J. Am. Chem. Soc.* **2012**, *134*, 9886-9889. X. Yu, A. Mailman, K. Lakin, A. Assoud, C. M. Robertson, B. C. Noll, C. F. Campana, J. A. K. Howard, P. A. Dube, R. T. Oakley, *J. Am. Chem. Soc.* **2012**, *134*, 2264-2275.
- [3] C. P. Constantinides, P. A. Koutentis, J. M. Rawson, *Chem. Eur. J.* **2012**, *18*, 7109-7116. R. I. Thomson, C. M. Pask, G. O. Lloyd, M. Mito, J. M. Rawson, *Chem. Eur. J.* **2012**, *18*, 8629-8633.
- [4] R. C. Haddon, *Nature* **1975**, *256*, 394-396. R. C. Haddon, *Aust. J. Chem.* **1975**, *28*, 2333-2342. R. C. Haddon, *Aust. J. Chem.* **1975**, *28*, 2343-2351.
- [5] W. K. Musker, T. L. Wolford, *J. Am. Chem. Soc.* **1976**, *98*, 3055-3056. W. K. Musker, P. B. Roush, *J. Am. Chem. Soc.* **1976**, *98*, 6745-6746. W. K. Musker, T. L. Wolford, P. B. Roush, *J. Am. Chem. Soc.* **1978**, *100*, 6416-6421. W. K. Musker, *Acc. Chem. Res.* **1980**, *13*, 200-206. T. G. Brown, A. S. Hirschon, W. K. Musker, *J. Phys. Chem.* **1981**, *85*, 3767-3771.
- [6] K.-D. Asmus, D. Bahnmann, Ch.-H. Fischer, D. Veltwisch, *J. Am. Chem. Soc.* **1979**, *101*, 5322-5329. K.-D. Asmus, *Acc. Chem. Res.* **1979**, *12*, 436-442.
- [7] F. Iwasaki, N. Toyoda, R. Akaishi, H. Fujihara, N. Furukawa, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2563-2567; H. Fujihara, T. Ninou, R. Akaishi, T. Erata and N. Furukawa, *Tet. Lett.*, **1991**, *32*, 4537-4540.
- [8] R. S. Glass, S. W. Andruski, J. L. Broeker, H. Firouzabadi, L. K. Steffen, G. S. Wilson, *J. Am. Chem. Soc.* **1989**, *111*, 4036-4045. R. S. Glass, L. Adamowicz, J. L. Broeker, *J. Am. Chem. Soc.* **1991**, *113*, 1065-1072.
- [9] R. S. Glass, J. L. Broeker, H. Firouzabadi, *J. Org. Chem.* **1990**, *55*, 5739-5746.
- [10] H. Fujihara, H. Ishitani, Y. Takaguchi, N. Furukawa, *Chem. Lett.* **1995**, *24*, 571-572.
- [11] F. Iwasaki, N. Toyoda, R. Akaishi, H. Fujihara, N. Furukawa, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2563-2567. K. George, M. Jura, W. Levason, M. E. Light, L. P. Ollivere, G. Reid, *Inorg. Chem.* **2012**, *51*, 2231-2240. D. H. Evans, N. E. Gruhn, J. Jin, B. Li, E. Lorance, N. Okumura, N. A. Macias-Ruvalcaba, U. I. Zakai, S.-Z. Zhang, E. Block, R. S. Glass, *J. Org. Chem.* **2010**, *75*, 1997-2009. G. M. de Oliveira, E. Faoro, E. S. Lang, *Inorg. Chem.* **2009**, *48*, 4607-4609. F. Iwasaki, M. Morimoto, M. Yasui, R.

- Akaishi, H. Fujihara, N. Furukawa, *Acta. Crystallogr. Sect. C* **1991**, *47*, 1463-1466.
- [12] P. Kilian, F. R. Knight, J. D. Woollins, *Chem. Eur. J.* **2011**, *17*, 2302-2328. P. Kilian, F. R. Knight, J. D. Woollins, *Coord. Chem. Rev.* **2011**, *255*, 1387-1413.
- [13] W. Nakanishi, S. Hayashi, S. Toyota, *Chem. Commun.* **1996**, 371-372. W. Nakanishi, S. Hayashi, A. Sakae, G. Ono, Y. Kawada, *J. Am. Chem. Soc.* **1998**, *120*, 3635-3640. W. Nakanishi, S. Hayashi, S. Toyota, *J. Org. Chem.* **1998**, *63*, 8790-8800. S. Hayashi, W. Nakanishi, *J. Org. Chem.* **1999**, *64*, 6688-6696. W. Nakanishi, S. Hayashi, T. Uehara, *J. Phys. Chem. A* **1999**, *103*, 9906-9912. W. Nakanishi, S. Hayashi, T. Uehara, *Eur. J. Org. Chem.* **2001**, 3933-3943. W. Nakanishi, S. Hayashi, *Phosphorus Sulfur Silicon Relat. Elem.* **2002**, *177*, 1833-1837. W. Nakanishi, S. Hayashi, T. Arai, *Chem. Commun.* **2002**, 2416-2417. S. Hayashi, W. Nakanishi, *J. Org. Chem.* **2002**, *67*, 38-48. W. Nakanishi, S. Hayashi, N. Itoh, *Chem. Commun.* **2003**, 124-125. S. Hayashi, H. Wada, T. Ueno, W. Nakanishi, *J. Org. Chem.* **2006**, *71*, 5574-5585. S. Hayashi, W. Nakanishi, *Bull. Chem. Soc. Jpn.* **2008**, *81*, 1605-1615.
- [14] F. R. Knight, A. L. Fuller, M. Bühl, A. M. Z. Slawin and J. D. Woollins, *Chem. Eur. J.*, **2010**, *16*, 7503-7516.
- [15] F. R. Knight, A. L. Fuller, M. Bühl, A. M. Z. Slawin, J. D. Woollins, *Chem. Eur. J.* **2010**, *16*, 7617-7634.
- [16] F. R. Knight, A. L. Fuller, M. Bühl, A. M. Z. Slawin, J. D. Woollins, *Chem. Eur. J.* **2010**, *16*, 7605-7616.
- [17] F. R. Knight, A. L. Fuller, M. Bühl, A. M. Z. Slawin, J. D. Woollins, *Inorg. Chem.* **2010**, *49*, 7577-7596.
- [18] L. K. Aschenbach, F. R. Knight, R. A. M. Randall, D. B. Cordes, A. Baggott, M. Bühl, A. M. Z. Slawin, J. D. Woollins, *Dalton Trans.* **2012**, *41*, 3141-3153.
- [19] F. R. Knight, K. S. Athukorala Arachchige, R. A. M. Randall, M. Bühl, A. M. Z. Slawin, J. D. Woollins, *Dalton Trans.* **2012**, *41*, 3154-3165.
- [20] F. R. Knight, R. A. M. Randall, K. S. Athukorala Arachchige, L. Wakefield, J. M. Griffin, S. E. Ashbrook, M. Bühl, A. M. Z. Slawin, J. D. Woollins, *Inorg. Chem.* **2012**, *51*, 11087-11097.
- [21] M.-L. Lechner, K. S. Athukorala Arachchige, R. A. M. Randall, F. R. Knight, M. Bühl, A. M. Z. Slawin, J. D. Woollins, *Organometallics* **2012**, *31*, 2922-2930.
- [22] M. Bühl, F. R. Knight, A. Křístková, I. Malkin Ondík, O. L. Malkina, R. A. M. Randall, A. M. Z. Slawin, J. D. Woollins, *Angew. Chem. Int. Ed.* **2013**, *52*, 2495-2498.
- [23] K. Wiberg, *Tetrahedron* **1968**, *24*, 1083-1096: WBIs, a measure for the covalent character of a bond, approaching WBI = 1 for a true single bond.
- [24] N. G. Connelly, W. E. Geiger, *Chem. Rev.* **1996**, *96*, 877-910.
- [25] P. Nagy, D. Szabó, I. Kapovits, Á. Kucsman, G. Argay, A. Kálmán, *J. Mol. Struct.* **2002**, *606*, 61-76.
- [26] F. R. Knight, R. A. M. Randall, L. Wakefield, A. M. Z. Slawin, J. D. Woollins, *Molecules* **2012**, *17*, 13307-13329. F. R. Knight, R. A. M. Randall, L. Wakefield, A. M. Z. Slawin, and J. D. Woollins, *Dalton Trans.* **2012**, *42*, 143-154.
- [27] S. Stoll, A. Schweiger, *J. Magn. Reson.* **2006**, *178*, 42-55.
- [28] A. L. Fuller, L. A. S. Scott-Hayward, Y. Li, M. Bühl, A. M. Z. Slawin, J. D. Woollins, *J. Am. Chem. Soc.* **2010**, *132*, 5799-5802

---

Received: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

## Entry for the Table of Contents (Please choose one layout)

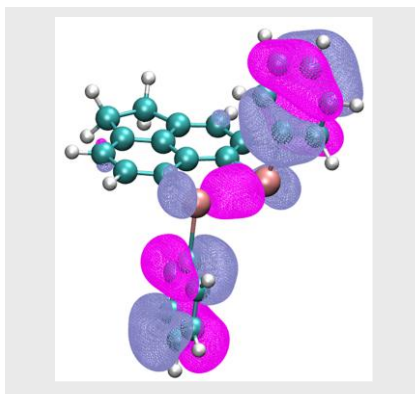
Layout 1:

## COMMUNICATIONS

---

### Chalcogen Dications

Facile synthesis of E-E bonded dications can be readily achieved. Radical cations are identified as the intermediates.



*Fergus R. Knight, Rebecca A. M. Randall, Tracey L. Roemmele, René T. Boéré, Bela E. Bode, Luke Crawford, Michael Bühl, Alexandra M. Z. Slawin and J. Derek Woollins [\*]*

**Electrochemically Informed Synthesis: Oxidation versus Coordination of 5,6-bis(phenylchalcogeno)acenaphthenes**