Odd-Electron-Bonded Sulfur Radical Cations: X-ray Structural Evidence of a Sulfur–Sulfur Three-Electron σ-Bond

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S *Supporting Information*

ABSTRACT: The one-electron oxidations of 1,8-chalcogen naphthalenes Nap(SPh)$_2$ (**1**) and Nap(SPh)(SePh) (**2**) lead to the formation of persistent radical cations **1**[•+] and **2**[•+] in solution. EPR spectra, UV–vis absorptions, and DFT calculations show a three-electron σ-bond in both cations. The former cation remains stable in the solid state, while the latter dimerizes upon crystallization and returns to being radical cations upon dissolution. This work provides conclusive structural evidence of a sulfur–sulfur three-electron σ-bond (in **1**[•+]) and a rare example of a persistent heteroatomic three-electron σ-bond (in **2**[•+]).

Much attention has been drawn to the chemistry of sulfur radical cations, not only because they are key intermediates in organic reactions and biological processes, but also for their important roles in materials science.[1] Generally, two classes of organic sulfur radical cations are observed: π-delocalized and p-localized. In the former class the unpaired electron is π-delocalized over one or more sulfur atoms containing heterocyclic rings, while in the latter the unpaired electron resides on sulfur 3p-orbitals. A number of π-delocalized sulfur radical cations have been isolated and structurally characterized,[1] such as thiophene radical cations.[2] In contrast, most of the p-localized radical cations (e.g., **A** and **B** in Scheme 1)

Scheme 1. p-Localized Sulfur Radical Cations
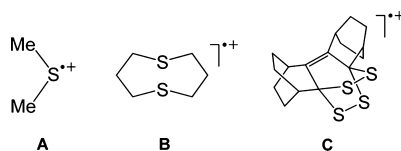
have been characterized only by EPR and UV–vis spectroscopies in matrix or in solution.[1] The only stable p-localized sulfur radical cation that has been isolated and characterized by X-ray crystallographic analysis is {2,3,5,6-tetrathiabicyclo[2.2.2]oct-7-ene}[•+] (**C** in Scheme 1), reported by Komatsu and co-workers,[3] where the unpaired electron is mainly delocalized over four sulfur atoms to form a four-center, seven-electron (4c-7e) bond.

Most of the p-localized sulfur radical cations (e.g., **B** in Scheme 1) exist in solution as species containing a three-electron σ-bond, formed by the interaction of a sulfur radical cation center with the p-type lone-pair electrons of another sulfur atom, with a bond order of 1/2 or less (Figure S1, Supporting Information (SI)). Three-electron σ-bonds, first described by Linus Pauling in the

1930s,[4] have been the subjects of considerable experimental and theoretical interest, and their importance as major intermediates is now well recognized.[5,6] However, only species containing cyclic framework-constrained N∴N or simple Xe∴Xe bonds have been isolated and structurally characterized by single-crystal X-ray diffraction (XRD).[7] Sulfur-centered radical cations are the typical models of three-electron σ-bonding and have been extensively studied in the gas phase, in solution, and in solid matrixes by various spectroscopic techniques[8,9] and theoretical calculations.[1a,6,10] Because there is no coupling between unpaired and nuclear spins for the two most abundant isotopes of sulfur, ^{32}S (94.9%, $I = 0$) and ^{34}S (4.29%, $I = 0$), the determination of structures by EPR is unconvincing. Crystal structure determination and analysis is a useful and direct method for studies of sulfur radical cations. However, due to instability, isolation of salts with a S∴S three-electron σ-bond remains a challenge.

We recently succeeded in stabilizing a number of interesting radical cations[2f,11] by using the weakly coordinating anion $[Al(OR_F)_4]^-$ ($OR_F = OC(CF_3)_3$).[12] Very recently, we isolated a radical cation of 1,8-bis(phenylselenyl)naphthalene (Nap-Se$_2$Ph$_2$[•+]) that features a Se∴Se three-electron σ-bond.[13] Owing to the importance of sulfur-involved three-electron σ-bonds, especially in biochemistry,[1a,9] we decided to isolate sulfur analogues of NapSe$_2$Ph$_2$[•+].[13] We herein report one-electron oxidations of 1,8-bis(phenylsulfur)naphthalene (NapS$_2$Ph$_2$, **1**) and 1-(phenylselenyl)-8-(phenylsulfanyl)naphthalene (Nap-(SPh)(SePh), **2**),[14] both of which afford persistent S∴S and S∴Se three-electron σ-bonded radical cations (Scheme 2) in solution, and the former remains in the solid state.

1 and **2** were synthesized by literature methods,[14] and their cyclic voltammetry (CV) in CH$_2$Cl$_2$ at room temperature with ^{n}Bu$_4$NPF$_6$ as a supporting electrolyte reveals reversible oxidation

Scheme 2. Sulfur Radical Cations Containing a S∴S or S∴Se Three-Electron σ-Bond
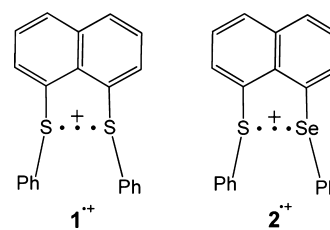
peaks (Figures S2 and S3, SI). Prompted by these CV data, **1** and **2** were treated with 1 equiv of $NO[Al(OR_F)_4]$[15] in CH_2Cl_2 to afford deep-colored solutions of radical cations **1**•+ (green) and **2**•+ (blue). The former keeps stable in the solid state, while the latter crystallizes out as a dimer, $[2-2]^{2+}$, upon concentration. Redissolving $[2-2]^{2+}$ in CH_2Cl_2 gave a solution with EPR and absorption spectra identical to those of **2**•+. The crystallization and dissolution demonstrate a reversible process between radical cation **2**•+ and dimer $[2-2]^{2+}$, as shown in Scheme 3. Salts

Scheme 3. Reversible Dimerization of 2•+ **by the Formation and Dissociation of a Se−Se Bond**
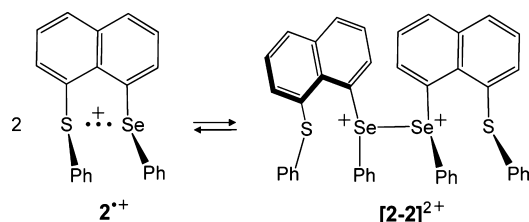
$1^{•+}[Al(OR_F)_4]^-$ and $[2-2]^{2+}·2[Al(OR_F)_4]^-$ are thermally stable under nitrogen atmosphere at room temperature and were studied by single-crystal XRD, EPR, UV−vis, NMR, and superconducting quantum interference device (SQUID) measurements, assisted by DFT calculations.

Crystals suitable for X-ray crystallographic studies were obtained by cooling solutions of $1^{•+}[Al(OR_F)_4]^-$ and $2^{•+}[Al(OR_F)_4]^-$ in CH_2Cl_2.[16] The structures of **1**•+ and $[2-2]^{2+}$ are shown in Figure 1, and some structural parameters of **1**•+ along
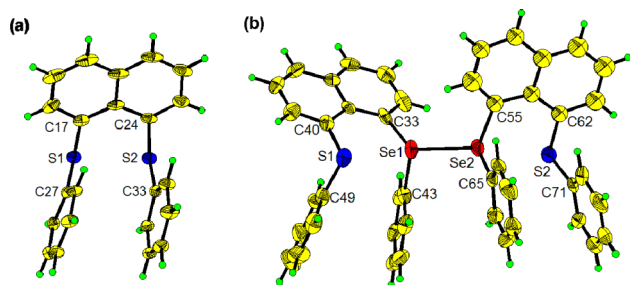
Figure 1. Thermal ellipsoid (50%) drawings of (a) **1**•+ and (b) $[2-2]^{2+}$. Yellow, C; green, H; red, Se; and blue, S. Selected bond lengths (Å) and angles (deg): in **1**•+, S1−C17 1.768(3), S1−C27 1.741(3), S2−C24 1.779(3), S2−C33 1.762(3), S1−S2 2.8168(11); C17−S1−C27 104.10(13), C24−S2−C33 103.45(13); in $[2-2]^{2+}$, S1−C40 1.793(11), S1−C49 1.765(11), Se1−C33 1.966(10), Se1−C43 1.911(9), Se1−Se2 2.7166(14), S2−C62 1.762(11), S2−C71 1.794(11), Se2−C55 1.931(10), Se2−C65 1.919(10), C40−S1−C49 103.3(5), C33−Se1−C43 103.3(4), C62−S2−C71 104.4(5), C55−Se2−C65 102.4(5), S1−Se1−Se2−S2 9.7.

with those of parent molecules **1** are given in Table S2 (SI). Radical cation **1**•+ is stacked as a dimeric pair (Figure S4, SI) by two weak $S···C_{nap}$ contacts (3.534 Å, ×2) that are close to the sum (3.60 Å) of van der Waals radii of sulfur and carbon. The phenyl rings overlap in a face-to-face offset arrangement with centroid−centroid distance (3.592(1) Å) within the range for typical $π−π$ stacking (3.3–3.8 Å). The phenyl rings are nearly parallel, with a small dihedral angle of 9.4°. The average C−S bond lengths are shorter while the ∠C−S−C angles are slightly larger than those in neutral **1**. The S···S separation (2.8168(11) Å) in **1**•+ is shorter than that (3.021(2) Å) in **1**. Single-crystal

XRD shows that the structure of $[2-2]^{2+}$ is composed of two subunits asymmetrically coupled through a selenium−selenium bond (2.7166(14) Å),[16b] giving rise to a nearly linear S−Se−Se−S arrangement (Figure 1b). The naphthalene planes of two units are perpendicular to each other.

To rationalize the experimental results, we carried out calculations for species **1**•+, **2**•+, and $[2-2]^{2+}$, along with parent molecules **1** and **2**.[17] Although the optimized geometry of **1**•+ at the UCAM-B3LYP/SVP level (a hybrid-DFT method, as the functional includes some Hartree−Fock exchange) has a S−S bond length of 2.814 Å, very close to that of its X-ray crystal structure, the phenyl rings bend away from each other (Table S2 and Figure S5c, SI). A satisfactory geometry of **1**•+ with nearly *cis*-"paralleled" phenyl rings was obtained at the UM06-2X/SVP level (Figure S5a, SI). Consistent with the experimental data, the one-electron oxidation causes a significant decrease of the S···S separation by 0.2−0.3 Å from **1** to **1**•+, which, combined with considerable spin density distribution (Figure 2a) on S atoms
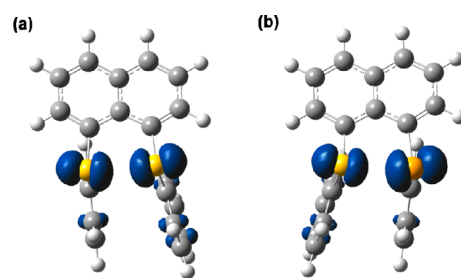
Figure 2. Spin density maps of **1**•+ (a) and **2**•+ (b) calculated at the UM06-2X/SVP level (isovalue = 0.006).

(0.40, 0.39), becomes strong evidence for the formation of a hemi bond between S atoms in **1**•+. The calculated bond order (Mayer 0.269, Wiberg 0.302 at UM06-2X/SVP; Mayer 0.294, Wiberg 0.325 at UCAM-B3LYP/SVP) for S−S further supports the hemi bond formation.[18] As shown in Figure S8 (SI), both sulfur atoms are main contributors to the singly occupied molecular orbital (SOMO), with S−S σ-antibonding character. To check whether the conformation affects the delocalization of electron spin density, a *trans*-conformer (Figure S5e, SI) that lacks the π−π interaction was also obtained at the same level. A shorter S−S bond (2.757 Å) and slightly larger spin densities on S (0.429, × 2) were observed for the *trans*-conformer. The π−π interaction between benzene rings of **1**•+ in the solid state is important for stabilization of the radical.

The calculated geometry of **2**•+ (Figure S6, SI) at the UM06-2X/SVP level is analogous to those of $NapSe_2Ph_2$•+ and **1**•+, with a Se−S bond order (Mayer 0.313, Wiberg 0.364) less than 0.5.[18] The spin density on Se (0.47) in **2**•+ (Figure 2b) is higher than those on Se (0.44) in $NapSe_2Ph_2$•+ and on S (0.40) in **1**•+, calculated at the UM06-2X/SVP level, which probably rationalizes the dimerization for **2**•+ but not for $NapSe_2Ph_2$•+ and **1**•+ with the $[Al(OR_F)_4]^-$ anion.[19] The crystal structure of the dimer $[2-2]^{2+}$ was theoretically reproduced as a closed-shell singlet at the M06-2X/SVP level. Of particular note, the calculated Se1−Se2 bond length (2.720 Å) is comparable to that (2.7166(14) Å) in the crystal structure of $[2-2]^{2+}$. The HOMO of $[2-2]^{2+}$ clearly shows a σ*−σ* interaction between SOMOs of two **2**•+ radical cations (Figure 3). In terms of valence bond theory, the S−Se−Se−S fragment in $[2-2]^{2+}$ may be viewed as a 4c-6e bonding stabilized by resonance structures, as shown in Figure S9 (SI).[20]
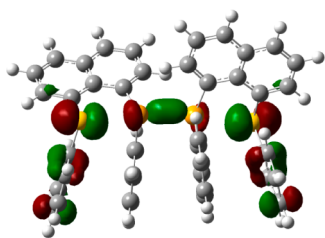
Figure 3. HOMO of $[2\text{-}2]^{2+}$, showing a $\sigma^*-\sigma^*$ interaction between two radical cation SOMOs (isovalue = 0.04).

The EPR spectrum (Figure 4a) of $1^{\bullet+}[\mathrm{Al(OR_F)_4}]^-$ solution at 298 K displays a seven-line signal due to coupling with six
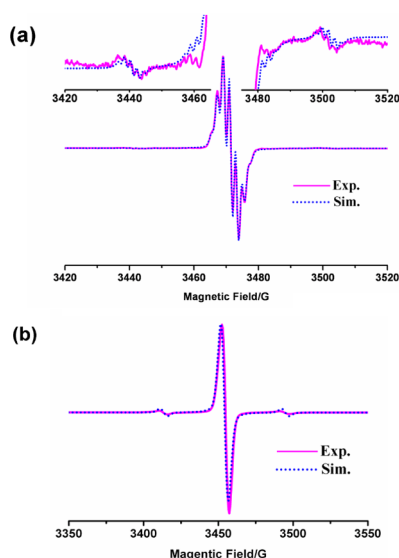
Figure 4. Experimental and simulated EPR spectra of 1×10^{-3} M solutions of (a) $1^{\bullet+}[\mathrm{Al(OR_F)_4}]^-$ and (b) $2^{\bullet+}[\mathrm{Al(OR_F)_4}]^-$ in CH_2Cl_2 at 273 K.

hydrogen atoms ($a(^1\mathrm{H}) = 1.8$ G) of the phenyl rings. The small coupling constant suggests a small amount of spin density on the carbon atoms, which is in agreement with DFT calculations (Tables S3 and S4, SI). Weak ^{33}S (spin $I = 3/2$; natural abundance = 0.76%) satellite quartet peaks with $a(^{33}\mathrm{S}) = 20.5$ G were observed and attributed to Nap^{33}SPhSPh species. The signal for the Nap^{33}SPh^{33}SPh isotopomer is too weak to observe because of its low concentration. The EPR spectrum of $2^{\bullet+}[\mathrm{Al(OR_F)_4}]^-$ solution at 298 K shows ^{77}Se (spin $I = 1/2$; natural abundance = 7.6%) satellite peaks, attributed to Nap^{77}SePhSPh species. The a_{iso} (81.3 G) is close to those for Me$_2$SeSeMe$_2^{\bullet+}$ (108 G) observed in γ-irradiated sample[21] and NapSe$_2$Ph$_2^{\bullet+}$ (95 G).[13] The EPR spectrum of crystalline $1^{\bullet+}[\mathrm{Al(OR_F)_4}]^-$ is anisotropic, with $g_x = 2.0005$, $g_y = 2.0055$, and $g_z = 2.0106$ (Figure S10, SI). The paramagnetic property of radical salt $1^{\bullet+}$ is further confirmed by the magnetic susceptibility (Figure S12, SI) and ^{1}H NMR silence (Figure S14, SI). The solid $[2\text{-}2]^{2+}([\mathrm{Al(OR_F)_4}]^-)_2$ exhibits an EPR spectrum (Figure S11, SI) similar to that observed for $1^{\bullet+}[\mathrm{Al(OR_F)_4}]^-$, but a SQUID measurement indicates that the solid is diamagnetic (Figure S13, SI), consistent with the dimer structure. The EPR signal of the solid is probably due to trace amounts of radical cation salt $2^{\bullet+}[\mathrm{Al(OR_F)_4}]^-$ trapped in the solid.

The UV–vis absorption spectra (Figure 5) of $1^{\bullet+}[\mathrm{Al(OR_F)_4}]^-$ and $2^{\bullet+}[\mathrm{Al(OR_F)_4}]^-$ solutions show two characteristic absorp-
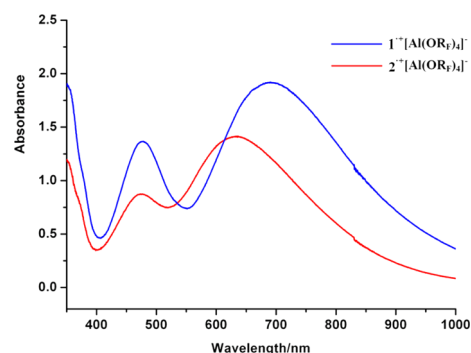
Figure 5. Absorption spectra of 1×10^{-4} M $1^{\bullet+}[\mathrm{Al(OR_F)_4}]^-$ and $2^{\bullet+}[\mathrm{Al(OR_F)_4}]^-$ in CH_2Cl_2 at 25 °C.

tions in the region of 370–680 nm for the reported absorptions of S∴S and Se∴Se bonds in the solution.[5e] The broad absorption peaks are typical of a three-electron σ-bond. In comparison to those of NapSe$_2$Ph$_2^{\bullet+}$ (465, 580 nm), the absorptions for $2^{\bullet+}$ (473, 636 nm) and $1^{\bullet+}$ (478, 690 nm) show a red shift. Judging from the time-dependent DFT (TD-DFT) calculations of radical cations $1^{\bullet+}$ and $2^{\bullet+}$, these absorptions are mainly assigned to HOMO (β) $\rightarrow$ LUMO (β) electronic transitions (Figures S18 and S19, SI).

We here have shown that the one-electron oxidations of 1,8-chalcogen naphthalenes lead to the formation of persistent radical cations $1^{\bullet+}$ and $2^{\bullet+}$ in the solution. EPR spectra, UV–vis absorption, and DFT calculations show that there are three-electron bonds in both cations. The former cation keeps stable in the solid state, while the latter crystallizes as a dimer. The contraction of the S···S distance in 1 upon oxidation supports the three-electron bond nature of $1^{\bullet+}$. This work thus provides conclusive structural evidence of a sulfur–sulfur three-electron σ-bond (in $1^{\bullet+}$) and a rare example of a persistent heteroatomic three-electron σ-bond (in $2^{\bullet+}$).[22] However, one should be aware that such three-electron bonds have been weakened to an extent by delocalization of partial electron spin density onto phenyl rings.[23] Further studies on chemical reactivity of these newly stabilized salts are under way.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Experimental section, crystallographic data in CIF formats, cyclic voltammograms, NMR spectra, SQUID measurements, calculated UV–vis absorption spectra, theoretical calculation details, and complete ref 17. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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(17) All calculations were performed using the Gaussian 09 program suite: Frisch, M. J.; et al. *Gaussian 09*, Revision B.01; Gaussian, Inc.: Wallingford, CT, 2010. See SI for geometries, coordinates, and full citation..

(18) The unpaired electron is partially delocalized on carbon atoms of phenyl rings (Tables S3 and S4, SI), leading to S−S and S−Se bond orders less than 0.5.

(19) $\mathrm{NapSe_2Ph_2}^{\bullet+}$ is shown to dimerize with a small anion, $\mathrm{SbF_6}^-$, in the solid state.[13]

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