Heteroleptic Samarium(III) Chalcogenide Complexes: Opportunities for Giant Exchange Coupling in Bridging σ- and π-Radical Lanthanide Dichalcogenides

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INTRODUCTION

The concept of Hard and Soft Acids and Bases (HSAB) presents a challenge for synthetic chemists aiming to bind heavy chalcogenics to f-elements, as there is a dichotomy between large and diffuse soft Lewis bases and highly electropositive hard f-block ions. For this reason, the chemistry of the f-block with sulfur, selenium, and tellurium has lagged behind that of their more congenial partner oxygen. However, it is precisely this hard/soft mismatch that makes lanthanide (Ln) chalcogenide complexes so appealing as paramagnetic centers, thus the inclusion of heavy chalcogenics with their radially extended p-orbitals is advantageous. The exchange interaction in Ln systems was often ignored until the arrival of a series of dilanthanide complexes bearing a highly reduced (N₂)₃ radical ligand that produced record high magnetic coupling between lanthanides to provide superior magnetic properties. Here, we show that heavy chalcogens (S, Se, Te) are primed to fulfill these criteria. The moderately reducing Sm(II) complex, [Sm(N₂)₃]₂⁺, where N₂ is the bulky bis(triisopropylsilyl)amide ligand, can be oxidized (i) by diphenyldichalcogenides EPh₂ (E = S, Se, Te) to form the mononuclear series [Sm(N₂)₃(EPh)] (E = S, 1-S2; Se, 1-Se₂; Te, 1-Te₂); (ii) S₈ or Se₈ to give dinuclear [{Sm(N₂)₃}(μ-η²-η²-E₂)] (E = S, 2-S₂; Se, 2-Se₂), or (iii) with Te=PET₃ to yield [{Sm(N₂)₃}(μ-Te)] (3). These complexes have been characterized by single crystal X-ray diffraction, multinuclear NMR, FTIR, and electronic spectroscopy; the sterically bulky N₂ dictates the formation of mononuclear complexes with chalcogenate ligands and dinuclear species with the chalcogenides. The Ln₇ fluorescent X-ray absorption spectra at the Sm L₃-edge yielded resolved pre-edge and white-line peaks for 1-S₂ and 2-E₂, which served to calibrate our computational protocol in the successful reproduction of the spectral features. This method was employed to elucidate the ground state electronic structures for proposed oxidized and reduced variants of 2-E₂. Reactivity is ligand-based, forming species with bridging superchalcogenide (E₂)₃ radical and subchalcogenide (E₂)₃ radical ligands. The extraordinarily large exchange couplings provided by these dichalcogenide radicals reveal their suitability as potential successors to the benchmark (N₂)₃ radicals in molecular magnets.

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ABSTRACT: The introduction of (N₂)₃ radicals into multinuclear lanthanide molecular magnets raised hysteresis temperatures by stimulating strong exchange coupling between spin centers. Radical ligands with larger donor atoms could promote more efficient magnetic coupling between lanthanides to provide superior magnetic properties. Here, we show that heavy chalcogens (S, Se, Te) are primed to fulfill these criteria. The moderately reducing Sm(II) complex, [Sm(N₂)₃]₂⁺, where N₂ is the bulky bis(triisopropylsilyl)amide ligand, can be oxidized (i) by diphenyldichalcogenides EPh₂ (E = S, Se, Te) to form the mononuclear series [Sm(N₂)₃(EPh)] (E = S, 1-S₂; Se, 1-Se₂; Te, 1-Te₂); (ii) S₈ or Se₈ to give dinuclear [{Sm(N₂)₃}(μ-η²-η²-E₂)] (E = S, 2-S₂; Se, 2-Se₂), or (iii) with Te=PET₃ to yield [{Sm(N₂)₃}(μ-Te)] (3). These complexes have been characterized by single crystal X-ray diffraction, multinuclear NMR, FTIR, and electronic spectroscopy; the sterically bulky N₂ dictates the formation of mononuclear complexes with chalcogenate ligands and dinuclear species with the chalcogenides. The Ln₇ fluorescent X-ray absorption spectra at the Sm L₃-edge yielded resolved pre-edge and white-line peaks for 1-S₂ and 2-E₂, which served to calibrate our computational protocol in the successful reproduction of the spectral features. This method was employed to elucidate the ground state electronic structures for proposed oxidized and reduced variants of 2-E₂. Reactivity is ligand-based, forming species with bridging superchalcogenide (E₂)₃ radical and subchalcogenide (E₂)₃ radical ligands. The extraordinarily large exchange couplings provided by these dichalcogenide radicals reveal their suitability as potential successors to the benchmark (N₂)₃ radicals in molecular magnets.

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Modifying the infrastructure to replace the highly reactive dinitrogen bridge with more tractable redox-active ligands has brought greater chemical versatility to these systems but has simultaneously diminished the exchange interaction as more atoms are added to the coupling pathway.\(^{14}\) Therefore, we propose dichalcogenides as potential successors to the dinitrogen ligand as they provide a single atom link and diffuse p orbitals that offer a more efficient coupling route.\(^{15}\) The most compelling attribute of dichalcogenides is their facile redox chemistry: the archetypal dichalcogenide \((E_2)^{2-}\) is readily reduced to the subchalcogenide oxidation level, \((E_2)^{3-}\), which is analogous to \((N_2)^{3-}\) but with a σ* magnetic orbital (Figure 1). Dichalcogenides can also be oxidized to superchalcogenides, \((E_2)^{n-}\), which are π-radical ligands that are isoelectronic with \((N_2)^{3-}\). Both of these radical species are stabilized through coordination to metal ions, as highlighted in a series of rigorous electronic structure studies recently reported by Berry et al.\(^{16–19}\)

Synthetic access to Ln heavy chalcogen species typically occurs by cleaving E=E bonds in chalcogen-containing compounds, which can be achieved by a Ln(II) reductant.\(^{20–23}\) Here, a series of low-coordinate Sm=E bonds are produced from the oxidation of \([\text{Sm}(N^{1+})_{2}]\) \((N^{1+} = \{\text{NSiPr}_{3}\})\)\(^{16–19,24,25}\) with (i) diphenyldichalcogenides \(E_2\text{Ph}_2\) \((E = S, Se, Te)\) to form the series \([\text{Sm}(N^{1+})_{2}\text{EPh}]\) \((E = S, Se, Te)\), (ii) \(E_2\text{S}_2\) or \(E_2\text{Se}_2\) and (iii) \(E_2\text{Te}\) to yield \([\text{Sm}(N^{1+})_{2}\text{(μ-TEPh)}]\) \((E = S, Se, Te)\), and (iii) \(E_2\text{TEt}_3\) to yield \([\text{Sm}(N^{1+})_{2}\text{(μ-TEt)}]\) \((E = S, Se, Te)\). Their molecular structures are confirmed by single-crystal X-ray diffraction, and electronic structures elucidated by a combination of spectroscopic and computational techniques. Exercising the methodology developed for the analogous halide series,\(^ {26}\) we employ the high resolution provided by fluorescence-detected X-ray absorption spectroscopy (XAS) to experimentally calibrate our density functional theoretical (DFT) method by canvassing a range of calculation parameters. The protocol that gave the best reproduction of the Sm L\(_3\)-edge by time-dependent (TD) DFT calculations was then applied to an examination of the one-electron oxidized and reduced variants of \(2\text{E}_2\text{EPh}\) \((E = S, Se)\), which contain \((E_2)^{2-}\) and \((E_2)^{3-}\) radical ligands, respectively. The analysis reveals the contrast between σ and π bridging radical ligands and shows both types afforded exchange couplings either equivalent to or greater than those seen in the \((N_2)^{3-}\) benchmarks. We also elaborate on the pivotal importance of the coligand in the design of new radical-bridged complexes with f elements.

### RESULTS AND DISCUSSION

**Synthesis.** The near-linear Sm(II) complex \([\text{Sm}(N^{1+})_{2}]\) was treated with a variety of oxidants in efforts to form homologous terminal Sm=EPh \((E = S, Se, Te)\) and bridged Sm\(_2\text{E}_n\) \((E = S, Se, Te; n = 1 or 2)\). Diallyl- and diaryl-dichalcogenides are commercially available sources of ER* as the E=E bond can be homolytically cleaved by two single electron transfer (SET) events, i.e., two Sm(II) ions can be oxidized to each gain a coordinated ER* unit. This methodology was previously employed to synthesize monomeric \([\text{Sm}(\text{Cp}*)_3\text{EPh}(\text{thf})]\) \((E = S, Se, Te)\) and dimeric \([\text{Sm}(\text{Cp}*)_2(\mu-\text{EPh})]\) \((E = S, Se, Te)\) complexes from either \([\text{Sm}(\text{Cp}*)_2\text{E}]\) \((E = S, Se, Te)\) or \([\text{Sm}(\text{Cp}*)_2(\mu-\text{EPh})]\) \((E = S, Se, Te)\).\(^ {21}\) There are numerous examples of analogous reactions across the f block,\(^ {20,23,27,28}\) and these polar M–ER groups \((M = \text{Ln} or \text{An})\) are amenable to further derivatization.\(^ {29}\) We have previously shown that although the ligand framework in \([\text{Sm}(N^{1+})_{2}]\) is sterically demanding, the two bis(trisopropylsilyl)amide ligands are flexible enough to bend toward each other to accommodate further moieties at the Sm center, thus we envisaged that this redox strategy would afford a series of structurally similar complexes.\(^ {32,26,30}\) Gratifyingly, the separate reactions of \([\text{Sm}(N^{1+})_{2}]\) with half an equivalent of \(E_2\text{Ph}_2\) in toluene gave the heteroleptic Sm(III) complexes \([\text{Sm}(N^{1+})_{2}\text{EPh}]\) \((E = S, Se, Te)\) and \([\text{Sm}(N^{1+})_{2}\text{EPh}(\text{thf})]\) \((E = S, Se, Te)\) \((\text{Scheme 1})\) in moderate to excellent yields (52–93%). Previously, Ln=EPh moieties have been investigated toward reductive elimination of \(E_2\text{Ph}_2\) in order to access Ln redox chemistry while avoiding the challenging synthesis of divalent precursors.\(^ {31}\)

The syntheses of mono- and polychalcogenido-bridged Sm(III) bis(trisopropylsilyl)amide complexes presented unexpected challenges. Using elemental sulfur in redox processes with f-block complexes is well-documented,\(^ {32–34}\) and the reaction of \([\text{Sm}(N^{1+})_{2}]\) with 1/4 of an equivalent of sulfur gave \([\text{Sm}(N^{1+})_{2}\text{(μ-η^2:η^2-S}_{2})]\) \(2\text{-S}_{2}\) in low yield \((\text{Scheme 2})\). The intended product based on stoichiometry was the monosulfido complex, thus the yield was not optimized. Attempts to furnish other \(E_2\) polyanions such as \(S_{2-}\) \(2–33,35\) or \(S_{2+}\) \(32,33,36\) by altering the stoichiometry only gave \(S_{2-}\) \([\text{Sm}(N^{1+})_{2}]\), and \(2\text{-S}_{2}\). The homologous diselenido-bridged

![Scheme 1. Synthesis of $[\text{Sm}(N^{1+})_{2}\text{EPh}]$ ($E = S, Se, Te$)](image)

![Scheme 2. Synthesis of $[\text{Sm}(N^{1+})_{2}\text{(μ-η^2:η^2-E}_{2})]$ ($E = S, Se$)](image)
Sm(III) complex \( \{[\text{Sm}(N^\text{III})_2]_2(\mu_\eta^2-\eta^2-S_2E_2)\} \) (2-SE) was also synthesized by treating \([\text{Sm}(N^\text{III})_2]_2\) with 1/4 of an equivalent of Se in similar yield to 2-Si (Scheme 2).

Reactions of \([\text{Sm}(N^\text{III})_2]_2\) with P(V) chalcogen atom transfer reagents E=PR(E=Ph, E=S, Se; R = Et, E = S, Se, Te)\(^\text{37}\) were uniformly sluggish, despite heating at 100 °C for several days (see Supporting Information). However, in one instance, prolonged heating of \([\text{Sm}(N^\text{III})_2]_2\) and Te=PEt\(_3\) gave single crystals of the monocobaltengido-bridged \([\{\text{Sm}(N^\text{III})_2\}]_2(\mu_\eta^2-\eta^2-S_2E_2)\) \(^\text{38}\) after standing for 2 weeks (Scheme 3).

Table 1. Room Temperature \( \chi_M \) Values (cm\(^3\) K mol\(^{-1}\)) Determined by Evans Solution NMR and Solid-State SQUID Magnetometry

|        | 1-S | 1-Se | 1-Te | 2-Si | 2-Se |
|--------|-----|------|------|------|------|
| Evans  | 0.37| 0.34 | 0.40 | 0.48 | 0.64 |
| SQUID  | 0.18| 0.14 | 0.19 | 0.35 | 0.46 |

**NMR Spectroscopy.** The \(^1\)H NMR spectra of 1-E each show two broad signals corresponding to the N\(^{\text{III}}\) ligand and were assigned based on integration. The methine peak positions shift downfield as the chalcogen electronegativity decreases (\(\delta_1 = 1-\text{S}, -8.61; 1-\text{Se}, -8.47; 1-\text{Te}, -8.30\) ppm), whereas the methyl peak positions are invariant (\(\delta_2 = 1-\text{S}, 0.24; 1-\text{Se}, 0.22; 1-\text{Te}, 0.21\) ppm). The proton resonances for the −EPh group in 1-E were not noticeably broadened by the paramagnetic Sm(III) center, with three peaks discernible for 1-S and 1-Te and the meta-protons in 1-Se masked by the solvent residual. The solution phase dynamics in 1-S were examined by monitoring the temperature dependence of the SPh proton resonances (Figure S40). The \(^{13}\)C\(^{\text{1H}}\) NMR spectra show two sharp peaks for the N\(^{\text{III}}\) ligand with the methine peak shifted upfield in the order of decreasing chalcogen electronegativity (\(\delta_1 = 1-\text{S}, 15.66; 1-\text{Se}, 15.55; 1-\text{Te}, 15.39\) ppm). The methyl peak was again invariant (\(\delta_2 = 1-\text{S}, 19.82; 1-\text{Se}, 19.77; 1-\text{Te}, 19.83\) ppm). The nonquaternary EPh resonances for 1-E were observed (\(\delta_1 = 1-\text{S}, 123.77, 128.68, 130.57; 1-\text{Se}, 123.77, 130.22, 134.97; 1-\text{Te}, 124.60, 129.91, 140.76\) ppm), with the peaks assigned to the ortho-C shifted upfield with decreasing chalcogen electronegativity. This trend has been noted in the related Sm(III) complexes \([\{\text{Sm}(\text{CP}^\text{III})_2(EPh)(\text{thf})\}]_2\).\(^\text{21}\) The \(^1\)H NMR spectra of 2-E\(_2\) contained multiple broad signals and could only be tentatively assigned due to their integrals being affected by the presence of diamagnetic HN\(^{\text{III}}\).

**Magnetometry.** Room temperature solution phase magnetic moments determined for 1-E and 2-E\(_2\) using the Evans method\(^\text{38}\) are consistent with other Sm(III)-N\(^{\text{III}}\) species (Table 1).\(^\text{24-26,30}\) The solution moments for 1-E are higher than the Sm−N distance shortens as the Sm−E distance increases, which is governed by the size of the chalcogenide (S\(^{2-}\), 1.84 Å; Se\(^{2-}\), 1.98 Å; Te\(^{2-}\), 2.21 Å). The incremental lengthening of the Sm−E bond on descent of group 16 is in excellent agreement with the related monomeric complexes \([\{\text{Sm}(\text{CP}^\text{III})_2(EPh)-(\text{thf})\}]_2\)\(^\text{††}\), although the analogous distances in 1-E are slightly shorter on account of their coordination number. The N−Sm−N angle is shifted significantly from 120° in all three complexes, though the magnitude decreases on descending the group (1-E, 138.33(7)°; 1-Te, 132.72(2)°; 1-Se, 128.61(1)°). The Sm−E−C angles also decrease from S to Te because of attenuated s-p hybridization in the frontier orbitals of the heavier chalcogens pushing the angle closer to 90°.\(^\text{41}\) The coordination spheres of 1-E are completed by several short C−H−Sm contacts, with the shortest Sm−C distances usually 3.1 Å. These interactions are ubiquitous in f-element complexes of these bulky bis(silyl)amide ligands and have been discussed in detail previously.\(^\text{26,30,42-44}\)

Complexes 2-S\(_2\) and 2-Se\(_2\) both crystallize in the P2\(_1/\)n space group with one molecule in the asymmetric unit. Both complexes feature two \([\{\text{Sm}(N^\text{III})_2\}]_2\) fragments linked by a \(\mu_\eta^2-\eta^2-\eta^2-E^2\) ligand (Figure 3), with E−E distances typical for S\(^{2-}\)(\(^\text{2}\) of 2.1075(10) Å and Se\(^{2-}\)(\(^2\) of 2.3662(7) Å constant with their diionic formulation.\(^\text{18,19}\) For example, in \([\{\text{Y}-(\text{N}^\text{III})_2(\text{thf})\}]_2(\mu_\eta^2-\eta^2-E^2)\) (N\(^\text{II}\) = \{N(SiMe\(_3\))\}_2; E = S, Se), the S−S distance is 2.118(2) Å and the Se−Se distance is 2.399(5) Å.\(^\text{53}\) The monodentate N\(^{\text{III}}\) ligands have Sm−N lengths that are typical for Sm(III) bond to this ligand (Table 3).\(^\text{36,39}\) The SmN\(_2\) units are canted relative to each other, with a dihedral angle (θ) between the mean planes of the terminal SmN\(_2\) groups residing at 45.8(1)° and 45.3(1)° for 2-S\(_2\) and 2-Se\(_2\), respectively. To the best of our knowledge 2-S\(_2\) represents the first structurally characterized example of a Sm\(_2\) unit despite several examples of Yb\(_2\)S\(_2\) species generated from similar reagents.\(^\text{53,45,46}\) The distinguishing features in 2-S\(_2\) are the long Sm−S distances, which are ca. 0.1 Å longer than in any related Ln\(_n\)S\(_2\) species.\(^\text{53,33,34,45-47}\) A recently reported Nd\(_2\)S\(_2\) complex has the same dimensions as the Sm\(_2\)S\(_2\) core in 2-S\(_2\)\(^\text{††}\) despite Nd(III) having a larger ionic radius.\(^\text{47}\) The long Sm−S bonds are the result of the steric demands of the N\(^{\text{III}}\) ligand, which limits the Sm−Sm distance to 5.273(1) Å. In
related compounds, the Ln···Ln separation is consistently below 5 Å, such that the distance in 2-S₄ represents the closest intermetallic separation permitted by the N†† ligand. We postulate that the considerable steric demands of N†† are responsible for analogous μ-N₂ species being unknown to date and the formation of a Sm₄(μ₃-O)₄ cubane in [{Sm(N††)₂}(μ₃-O)₄]₅⁻ rather than (μ-O₂)⁻⁻ ligands. Complex 2-Se₂ has an analogous structure, though the larger Se atoms with greater p character produce more acute Sm−E−Sm angles (133.13(2)°) and larger E−Sm−E angles (66.56(2)°) than found in 2-S₂ (Table 3). The dimension of the strictly planar Sm₂Se₂ unit in 2-Se₂ is identical to that in [{Sm(Cp*)₂}(μ-

Table 2. Selected Bond Distances (Å) and Angles (deg) for 1-E

|          | 1-S       | 1-Se      | 1-Te*    |
|----------|-----------|-----------|----------|
| Sm−E     | 2.6671(7) | 2.8458(10)| 3.1020(5) |
| Sm−Navg  | 2.321(2)  | 2.317(6)  | 2.303(4)  |
| N−Sm−N   | 138.33(7) | 132.7(2)  | 128.6(1)  |
| N−Sm−Eavg| 110.72(5) | 113.5(2)  | 115.6(1)  |
| Sm−E−C   | 120.45(9) | 115.1(2)  | 104.1(2)  |
| Sm−N₁Eₐₜₐₚ | 0.065(1) | 0.074(3)  | 0.082(2)b |

*Taken from molecule A in the asymmetric unit. The Sm ion in molecule B resides 0.066(2) Å above the plane, thus the trend is not definitive.

On one occasion, we obtained a polymorph of 2-S₂ that crystallized in a triclinic space group, which we include here as 2-S₂-polymorph (Figure S2). The structural features of 2-S₂-polymorph differ from 2-S₂ as it comprises two orientations of

Table 3. Selected Bond Distances (Å) and Angles (deg) for 2-E₂

|          | 2-S₂      | 2-Se₂     |
|----------|-----------|-----------|
| Sm−Eₐₜₐₚ | 2.8394(7) | 2.9749(6) |
| Sm−Navg  | 2.340(2)  | 2.331(4)  |
| E−E      | 2.1075(10)| 2.3662(7) |
| Sm−Sm    | 5.273(1)  | 5.459(2)  |
| Sm−E−Smₐₜₐₚ | 136.42(3) | 133.13(2) |
| Sm−E−Eₐₜₐₚ | 68.22(3)  | 66.56(2)  |
| E−Sm−E   | 43.58(2)  | 46.87(2)  |
| α        | 0.8(2)    | 0.3(1)    |
| θ        | 45.8(1)   | 45.3(1)   |

*Dihedral angle between mean SmE₂ planes. bDihedral angle between mean SmN₃ planes.

Figure 2. Molecular structures of [Sm(N††)₂(SPh)] (1-S, left), [Sm(N††)₂(SePh)] (1-Se, center), and [Sm(N††)₂(TePh)] (1-Te, right) with partial atom labeling. Displacement ellipsoids set at 30% probability level with hydrogen atoms are omitted for clarity.

Figure 3. Molecular structures of [{Sm(N††)₂}(μ-η²:η²-S₂)] (2-S₂, left) and [{Sm(N††)₂}(μ-η²:η²-Se₂)] (2-Se₂, right) with partial atom labeling. Displacement ellipsoids set at 30% probability level, and hydrogen atoms are omitted for clarity.

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the central Sm$_2$S$_2$ core with respect to the terminal SmN$_2$ moieties (Figure S3). The bond distances of 2-S$_2$-polymorph are essentially identical to 2-S$_2$, though the former exhibits a nearly parallel alignment of the two SmN$_2$ planes with $\theta = 4.6(1)^\circ$ (cf. 45.8(1)$^\circ$ for 2-S$_2$; Table S5).

In contrast to the diatomic bridges in 2-S$_2$ and 2-Se$_2$, the Sm centers in complex 3 are linked by a $\mu$-Te ligand (Figure 4).

![Figure 4](image)

**Figure 4.** Molecular structure of [(Sm(N$_2$)$_2$)$_2$(\(\mu\)-Te)] (3) with partial atom labeling. Displacement ellipsoids set at 30% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths: Sm(1)-Te(1) 2.9485(5) Å, Sm(2)-Te(1) 2.9461(5) Å, Sm(1)-N(1) 2.314(5) Å, Sm(1)-N(2) 2.327(5) Å, Sm(2)-N(3) 2.325(5) Å, Sm(2)-N(4) 2.334(5) Å, Sm(1)--Sm(2) 5.894(1) Å. Selected bond angles: Sm(1)-Te(1)-Sm(2) 178.64(2)$^\circ$, N(1)-Sm(1)-N(2) 134.2(2)$^\circ$, N(3)-Sm(2)-N(4) 135.7(2)$^\circ$.

The Sm-Te distances at 2.9461(5) and 2.9485(5) Å are not significantly different from the Sm-Se distances in 2-Se$_2$, but the periodic trend with increasing chalcogen radius is observed in the Sm---Sm distance of 5.894(1) Å. Sm---Te-Sm complexes are rare, with [(Sm(Cp$^*$)$_2$(thf)$_2$]$\mu$-Te)] being the only directly comparable complex; its longer Sm---Te bond of 2.993(2) Å likely reflects the higher coordination number. The two SmN$_2$ planes in 3 are almost coplanar ($\theta = 6.4(1)^\circ$), which results from crystal packing, as the same metric in 2-S$_2$ is 45.8(1)$^\circ$ but only 4.6(1)$^\circ$ in 2-S$_2$-polymorph (Table S5). Changes in the cationic in these moieties have been observed previously when bridging fragments get larger.$^{35}$

**Electronic Spectroscopy.** Electronic absorption spectra of 1-E and 2-E$_2$ were recorded as toluene solutions at ambient temperatures. The spectral overlay presented in Figure 5 highlights the similar profiles of the 1-E series, which are dominated by a broad feature tailing in from the UV region. This results from ligand-to-metal charge transfer (LMCT) processes; each features an absorption maximum at ca. 26 000 cm$^{-1}$, which imubes 1-S and 1-Se with their yellow-orange hue. The slightly darker tone to 1-Te stems from the additional peak at 18 150 cm$^{-1}$ with the spectral intensities trending 1-Te > 1-S > 1-Se. All three complexes exhibit identical features in the NIR region, with two well-resolved sharp peaks at 7725 and 7710 cm$^{-1}$, and one broad peak with a shoulder in the range 8373--8395 cm$^{-1}$. These features are characteristic of $^4H_{15/2} \rightarrow ^4F_{11/2,9/2,7/2}$ transitions based on comparisons with solid-state measurements of Ln(III) ions.$^{32}$ The spectrum of 2-S$_2$ shows the same LMCT band at 26 000 cm$^{-1}$ and an additional peak at 21 000 cm$^{-1}$ (Figure S60). The fingerprint profile in the NIR shows the same three bands as for the 1-E series, although slightly blue-shifted, suggesting an identical coordination geometry for the two Sm(III) ions in 2-S$_2$. On the other hand, 2-Se$_2$ possesses a featureless envelope of LMCT transitions in the range 21 000--29 000 cm$^{-1}$ but a sharper suite of fingerprint transitions that are red-shifted by ~200 cm$^{-1}$ (Figure S60). This profile likely stems from the presence of two Sm(III) ions with slightly different coordination geometry given the increased flexibility of the coordination sphere, which is not beholden to intramolecular interactions of the N$^{1+}$ coligands.

**X-ray Absorption Spectroscopy.** The electronic structures of 1-S, 2-S$_2$, and 2-Se$_2$ were examined using X-ray absorption spectroscopy (XAS) at the Sm L$_3$-edge. With a measurement energy of ca. 6720 eV, these spectra are not affected by electronic effects inherent to highly anisotropic ions that complicate many other techniques. The L$_3$-edge spectrum is dominated by a white-line peak composed of dipole-allowed 2p $\rightarrow$ 6s and 2p $\rightarrow$ 5d transitions.$^{33}$ For Ln ions with valence electrons residing in the 4f-subshell, dipole forbidden but quadrupole-allowed 2p $\rightarrow$ 4f electronic transitions constitute the pre-edge region at the base of the white-line peak.$^{35}$ These features are rarely observed in transmission experiments as they are buried beneath the white line, therefore we utilize fluorescence-detection to resolve the pre-edge peaks. Experimental spectra are compared in Figure 6, and pre-edge and white-line energies and intensities are listed in Table 4. The white-line energies across the series are essentially invariant, falling into the range 6722.7 ± 0.1 eV, with 2-S$_2$ and 2-Se$_2$ at slightly higher energies. These energies are identical to Sm L$_3$-edge energies recorded for related series [Sm(N$^{1+}$)$_2$X] (X = F, Cl, Br, I), which ranged 6722.5--6723.1 eV.$^{26}$ The enhanced resolution of the L$_3$ fluorescence spectrum yielded resolved pre-edge features for each compound, manifesting as two shoulder peaks at the base of the white line (Figure 6 inset). The first pre-edge is shifted 0.4 eV to higher energy for 2-Se$_2$ following the observation of higher energy with increasing size of the donor atom;$^{36,35}$ the second peak is constant at 6716.1 ± 0.1 eV. The pre-edge peaks reside ca. 10 eV below the white line, similar to the halide series,$^{36}$ as well as high-resolution studies performed on Ce$_2$(CO$_3$)$_3$ at 8.5 eV and Yb$_2$O$_3$ at 10.2 eV, to select two elements at either end of the Ln series.$^{36}$

![Figure 5](image)

**Figure 5.** Overlay of the electronic spectra of 1-E (E = S, Se, Te) as 1 mM solutions in toluene recorded at ambient temperature. Inset shows expansion of the NIR region.
The L3-edge spectrum measured the spin polarization at these lanthanide complexes unattainable. However, reproduction of contracted 4f-subshell renders a similar quantification height, in arbitrary units. Paramagnetic centers, i.e., the difference in energy between α-spin (spin-up) and β-spin (spin-down) 4f orbitals, as well as the position of the 5d manifold. Using the Sm L3-edge spectrum of 1-S as a reference point, we screened a suite of functionals and basis sets to select the best combination that match the experiment. Calculation of the L3-edge spectrum of 1-S was carried out on the crystallographic coordinates of the molecule. For a given theoretical method—functional and basis set—an empirical correction is applied to the calculated Sm L3-edge spectrum to align it with the experimental data highlighting the effect of the calculation parameters on the ground state electronic structure. The chosen functionals PBE, PBE0, BHandHLYP, and M062X are listed in order of increasing Hartree–Fock (HF) exchange of 0%, 16%, 25%, 50%, and 54%, respectively.

A comparison of the calculated Sm L3-edge was made with the bespoke segmented all-electron relativistically contracted (SARC) basis set for Sm. This compact basis set was used for the calculation of the corresponding halide series [Sm(NX)2] (X = F, Cl, Br, I) and underestimated the 4f–5d energy gap by 4 eV with the PBE0 functional. With the SARC-ZORA-TZVP basis set, the BHandHLYP functional gave the best match, with a pre-edge splitting of 4.5 eV and first pre-edge peak position 11.2 eV below the white line (Figure S69). Overall, the PBE0/ZORA-def2-TZVP combination gave the best result and was applied to the calculation of the Sm L3-edge of 2-S2 and 2-Se2. For these compounds, the calculated spectra were normalized and overlaid with that of 1-S (Figure 7). Overall, the calculated spectra are in very good agreement with the experiment, with the relative energy and relative intensity of the two pre-edge peaks well reproduced (Table 4). Where the calculated spectrum diverges from the experimental one above 6716 eV marks the start of the dominant white-line peak whose line width differs from the pre-edge features and is difficult to model with the uniform line width and Gaussian line shape output from the calculations.

The performance of each functional was assessed by the splitting of the two pre-edge peaks and their position relative to the white line. The most accurate reproduction was achieved with the PBE0 hybrid functional (25% HF), with a pre-edge splitting energy of 2.9 eV and first pre-edge peak position 9.0 eV below the white line compared with the experimental values of 3.4 and 10.0 eV, respectively (Table 4). The remaining functionals followed the trend of increasing energy splitting with increasing HF exchange (Table S7). The improved resolution provided by detection of the Lo fluorescence line gave two well-defined pre-edge peaks that result almost entirely from quadrupole-allowed 2p → 4f transitions. The first comprises the excitation of a spin-up electron to the two pre-edge peaks well reproduced (Table 4). Where the calculated spectrum diverges from the experimental one above 6716 eV marks the start of the dominant white-line peak whose line width differs from the pre-edge features and is difficult to model with the uniform line width and Gaussian line shape output from the calculations.

Theoretical Calculations. Ground State Electronic Structure. Our previous study on low-coordinate Sm(III) complexes utilized a simple time-dependent (TD) DFT method to reproduce the experimental X-ray absorption spectra. Typically, this approach has been used to evaluate covalency in a suite of d-block complexes, but the contracted 4f-subshell renders a similar quantification in lanthanide complexes unattainable. However, reproduction of the L3-edge spectrum measured the spin polarization at these paramagnetic centers, i.e., the difference in energy between α- and β-electrons.

Table 4. Experimental and Calculated Sm L3-edge XAS Data

| Compound | Pre-edge Energy (eV) | Intensity | White-line Energy (eV) | Intensity |
|----------|----------------------|-----------|------------------------|-----------|
| 1-S      | 6712.6 (6713.6)      | 0.08      | 6722.6 (6722.6)        | 10.8      |
| 2-S2     | 6716.0 (6716.5)      | 0.27      | 6722.7 (6722.7)        | 14.6      |
| 2-Se2    | 6713.0 (6713.4)      | 0.10      | 6722.8 (6722.7)        | 10.5      |

*Calculated (PBE0/def2-TZVPP) values in parentheses are shifted −193.6 eV. Energy of minimum in second derivative spectrum. Pre-edge peak height, in arbitrary units. Area under the single Gaussian fit to the white-line peak after subtraction of the edge, in arbitrary units.

Figure 6. Comparison of the normalized Sm L3-edge XAS (top) and their FFT-smoothed second derivative spectra (bottom) for 1-S, 2-S2, and 2-Se2 recorded at 100 K. Insets show expansion of the overlaid FFT-smoothed pre-edge peak (top) and their second derivative (bottom).
comprises excitations to the seven unoccupied $\beta$-spin f orbitals of the Sm(III) ion (Figures S70−S72). The difference in energy of the two pre-edge peaks is a measure of the polarization of the valence orbitals, which stabilizes the $\alpha$-spin f orbitals relative to their $\beta$-spin counterparts by 3.4, 3.5, and 3.2 eV in 1-S, 2-S$_2$, and 2-Se$_2$, respectively (Table 4). This effect also manifests in the Mulliken spin population analysis leading to more than five unpaired spins at the Sm ion, which increases with increasing size of the chalcogen (Figure S73). This is brought about by a poorer energy match of the 4f-manifold with the np orbitals of the chalcogen such that Se 4p and Te 5p orbitals are energetically closer to the Sm 5d orbitals,28,46,66

Figure 7. Comparison of the experimental (top) and calculated (bottom) Sm L$_3$-edge spectra for 1-S (red), 2-S$_2$ (blue), and 2-Se$_2$ (orange) obtained from PBE0/ZORA-def2-TZVPP TD-DFT calculations. Calculated spectra are shifted −193.6 eV with a 3 eV line broadening. The left panel shows expansion of the pre-edge region with the solid line depicting the experimental data and the dashed line, the calculated pre-edge spectrum. Calculated stick plot spectra are shown in Figures S70−S72.

Exchange Coupling via Bridging Radicals. The potential of dichalcogenide radicals to mediate exchange interactions within dilanthanide complexes can be measured by the magnitude of their isotropic exchange coupling constants ($J$), as defined by the spin-Hamiltonian shown in eq 1. Broken symmetry DFT calculations have proven effective at estimating the Ln−radical ($J_{\alpha\alpha}$) and Ln−Ln ($J'_{\alpha\alpha}$) coupling constants in the $[\text{Ln}(N^\text{″})_2(\text{thf})]_2(\mu-\eta^2-\eta^2-N_2)$− (Ln = Gd, Tb, Dy, Ho, Er) series,13,67,68 especially for the anisotropic ions where such parameters are difficult to measure experimentally, including Sm. The difference in the total energies for the high-spin (HS) and broken symmetry (BS) electronic solutions gives reliable estimates for $J_{\alpha\alpha}$ and $J'_{\alpha\alpha}$ using the preferred nonspin-projected approach defined in eqs 2 and 3.69 The veracity of this method was calibrated for the gadolinium species as the $^8$S ion is devoid of contributions from spin−orbit coupling.13,67,68 The experimentally validated PBE0/ZORA-def2-TZVPP protocol was used to calculate the ground state electronic structures of 2-S$_2$ and their one-electron oxidized and reduced species. The computed $J$ values are benchmarked by comparing to those calculated for $[\text{Gd}(N^\text{″})_2(\text{thf})]_2(\mu-\eta^2-\eta^2-N_2)$ and $[\text{Gd}(N^\text{″})_2(\text{thf})]_2(\mu-\eta^2-\eta^2-N_2)$−. Using our theoretical procedure, we have calculated the exchange coupling between the Gd(III) ions in $[\text{Gd}(N^\text{″})_2(\text{thf})]_2(\mu-\eta^2-\eta^2-N_2)$ at $J'_{\alpha\alpha} = −0.32$ cm$^{-1}$, which is a good match to the experimental value of $−0.49$ cm$^{-1}$10 and similar to other DFT-derived estimates ($−0.53$ cm$^{-1}$ and $−0.33$ cm$^{-1}$).67,68 Such a miniscule value reflects the large separation between the Gd(III) ions such that they are uncoupled paramagnetic centers.

Figure 8. Qualitative MO scheme for the [2-S$_2$]$^{0/0+}$ electron transfer series showing relative energies of the frontier orbitals derived from DFT calculations. Singly occupied MOs are denoted with red and blue arrows for $\alpha$-spin and $\beta$-spin electrons, respectively. $\Delta_\sigma$ and $\Delta_\pi$ are the energy gaps between the 4f manifold and the ligand-based $\sigma^*$ (b$_{2u}$) and $\pi^*$ (b$_{1g}$) MOs, respectively (in $D_2h$ symmetry). Below are presented the Mulliken spin population analyses (red, $\alpha$-spin; yellow, $\beta$-spin).
\[ \hat{H} = -2J_{\text{ex}}^\text{fi} \hat{S}^\text{fi}_\text{Sm1} \cdot \hat{S}^\text{fi}_\text{Sm2} - 2J_{\text{ex}}^\text{de} \hat{S}^\text{de}_\text{Sm1} \cdot \hat{S}^\text{de}_\text{Sm2} \]  
(1)

\[ J_{\text{ex}}^\text{fi} = (E_{\text{BS1}} - E_{\text{HS1}})/12 \]  
(2)

\[ J_{\text{ex}}^\text{de} = [(E_{\text{BS2}} - E_{\text{BS1}}) + J_{\text{ex}}^\text{ff}]/30 \]  
(3)

Geometry optimization of 2-S2 and 2-Se2 was started from their crystallographic coordinates. The bulky N\textsuperscript{17} ligands were trimmed to the N\textsuperscript{-} sized variant in order to speed up the calculations. These simplified structures do not significantly alter the underlying electronic structure like the ground state electronic structure as measured by orbital energies and composition, and overlap integrals of the paramagnetic centers are unchanged. There are noticeable differences in the geometries, which is a consequence of lifting the steric demands of the N\textsuperscript{17} ligands in these truncated models (see SI for details). The ground state electronic structures of 2-S2 and 2-Se2 models were computed at the PBE0/ZORA-def2-TZVPP level of DFT. A broken-symmetry BS(S,S) calculation gives five \( \alpha \)-spin SOMOs on one Sm(III) ion and five corresponding \( \beta \)-spin SOMOs on the other Sm(III) ion (Figure 8). The large intermetal separation ensures there is no overlap of magnetic orbitals, with the overlap integral \( S \approx 0 \). The 4f orbitals are nestled between the two occupied \( \pi^* \) MOs of the disulphide, which transform as \( b_3g \) and \( b_{2g} \) in \( D_{3h} \) symmetry, and the unoccupied \( \sigma^* \) (\( b_{3g} \)) MO, which confers a bond order of 1. The Mulliken spin population analysis gives more than five spins at Sm due to the aforementioned spin polarization.

The Sm--Sm exchange coupling constants \( J_{\text{ex}}^\text{de} \) in 2-S2 and 2-Se2 are estimated at \(-0.94 \) and \(-0.71 \) cm\textsuperscript{-1}, respectively. The coupling is slightly larger than the corresponding value computed for \([\{\text{Gd(N}^\text{3+})_2(\text{thf})_2\}_2(\mu-\eta^2-\eta^2-N_2)]\) \( J_{\text{ex}}^\text{de} = -0.32 \) cm\textsuperscript{-1}, indicating a slightly more efficient superexchange pathway is produced by larger donor atoms. Interestingly, \( J_{\text{ex}}^\text{de} \) calculated on the solid state structures of 2-S2 and 2-Se2 is smaller in magnitude and weakly ferromagnetic, with values of \(+0.54 \) and \(+0.07 \) cm\textsuperscript{-1}, respectively. We ascribe this difference to the nonplanarity of the Sm 2E2 unit in the optimized structures giving shorter Sm--E and Sm--Sm distances than in the solid state. The distortion of the diamond core has been shown to induce a positive shift in the exchange coupling constant,\textsuperscript{67,68} though we note a shift of ca. 1 cm\textsuperscript{-1} is largely insignificant.

The addition of an electron to the 2-S2 model generates a monoanionic compound with two Sm(III) ions linked through a bridging sulphide, (S\textsubscript{2})\textsuperscript{3−}. The locus of the redox event is clearly indicated by the lengthening of the S--S distance to 3.254 Å, commensurate with a two-center/three-electron bond.\textsuperscript{17} Berry and co-workers have catalogued all structurally characterized compounds with sulffide ligands and showed for second and third row d-block metals that the S--S distance ranges from 2.9--3.1 Å.\textsuperscript{19} Although the S--S distance in the 2-S2\textsuperscript{3−} model lies just outside this interval, it is shorter than the nonbonded sulhide distance of over 3.5 Å in \([\{\text{Zr(Cp)}_2\}_2(\mu-S\textsubscript{2})]_2\). The Sm--Sm separation decreases by ca. 1 Å as the fold along the S--S vector increases to 40.5° (Table S15). The decrease in the intermetal separation is diagnostic of ligand-centered reduction as the Sm--S--Sm angle approaches 90° in order to accommodate the shorter Sm--S distance driven by electrostatic attraction with the trionic bridging ligand. Therefore, the bulk of the N\textsuperscript{17} ligands is likely preventing the formation of the monoanionic species by restricting the Sm ions from adopting a disposition that stabilizes the bridging sulphide group. This observation is in line with the current absence of any Ln\textsuperscript{17}(\( \mu-\eta^2-\eta^2\)-N\textsubscript{2}) compound with N\textsuperscript{17}, hence N\textsuperscript{−} ligands are necessary to achieve convergence of the optimized 2-S2\textsuperscript{3−} species. A BS(10,1) calculation revealed that the \( M_x = 9/2 \) state (identified as BS1) is 1.5 kcal mol\textsuperscript{-1} more stable than the high-spin (HS) solution. This ground state consists of parallel alignment of the 10 unpaired electrons from the Sm(III) ions that are antiferromagnetically coupled to the unpaired spin of the sulphide (Figure 8). The reduced ligand, although bearing the same charge as the dinitrogen analogues, has its unpaired electron in a \( \pi^* \) (\( b_{3g} \)) MO, in contrast to the \( \sigma^* \) (\( b_{3g} \)) SOMO in \((\text{N}^\text{2})^3\)\textsuperscript{−}.\textsuperscript{13,67,68} The alternative scenario is antiferromagnetic coupling between terminal Sm(III) ions leading to a net \( M_x = 1/2 \) state (denoted BS2). Addition of an electron to the ligand creates a \( \sigma^* \) SOMO which has a small overlap (\( S = 0.17 \)) with the corresponding magnetic orbital in the \( \alpha \)-spin manifold being the \( f_\alpha \) orbital (Table 5). Although the exchange interaction is larger than calculated for the \((\text{N}^\text{2})^3\)\textsuperscript{−} series,\textsuperscript{67,68} it is relatively weak, with largely electrostatic bonding given the 82% S 3p character in this \( \beta \)-spin SOMO (Table S21). The composition of the \( \sigma^* \) MO is unchanged from the neutral complex and consistent with bond covalency derived from \( E_{\text{np}}-L_n \) 5d overlap.\textsuperscript{71} The Mulliken spin analysis locates more than five spins on each Sm(III) ion and more than one spin on the sulphide unit.

Using total energies for the HS, BS1, and BS2 states, the Sm--radical and Sm--Sm exchange coupling constants for the 2-S2\textsuperscript{3−} model are estimated at \(-33.9 \) cm\textsuperscript{-1} and \(+7.0 \) cm\textsuperscript{-1}, respectively. Considering the aforementioned functional and basis set dependency for calculated parameters, we calculated the corresponding parameters for \([\{\text{Gd(N}^\text{3+})_2(\text{thf})_2\}_2(\mu-\eta^2-\eta^2-N_2)]^+\) at \( J_{\text{ex}} = -35.2 \) cm\textsuperscript{-1} and \( J_{\text{ex}} = +2.9 \) cm\textsuperscript{-1}. There is good agreement with the experimental \( J_{\text{ex}} \) value of \(-27 \) cm\textsuperscript{-1}, though the \( J_{\text{ex}} \) value is overestimated given the experimental result of \(-0.49 \) cm\textsuperscript{-1}.\textsuperscript{10} Comparing the two bridging ligands, (S\textsubscript{2})\textsuperscript{3−} and (N\textsubscript{2})\textsuperscript{3−}, the \( J_{\text{ex}} \) values are the same but the \( J_{\text{ex}} \) coupling is twice the magnitude for the sulphide ligand. This follows the trend observed for the nonradical (S\textsubscript{2})\textsuperscript{2−} ligand with the analogous (N\textsubscript{2})\textsuperscript{2−} species (vide supra). The salient difference provided by the dichalocgenido bridge and the (N\textsubscript{2})\textsuperscript{3−} analogues is the small energy gap (\( \Delta_x \)) between the corresponding magnetic orbitals being an order of magnitude smaller for the 2-S2\textsuperscript{3−} model. This has the effect of supplying a greater contribution from promotion energy of electron transfer to the exchange interaction because the paramagnetic ions more efficiently overlap through the dichalocgenide ligand.\textsuperscript{13} This offsets the diminished contribution from direct exchange, and delocalization of unpaired electrons (i.e., covalency) of the larger Sm2S2 core. The bond metrics in

Table 5. Calculated Exchange Coupling Constants (J (cm\textsuperscript{-1})), Energy Gaps (\( \Delta \) (cm\textsuperscript{-1})), and Orbital Overlap Integrals (S) (S

\[
\begin{array}{cccccc}
\text{2-S2}^+ & \text{2-S2}^- & \text{2-Se2}^+ & \text{2-Se2}^- & \text{2-Se2}^+ & \text{2-Se2}^-
\end{array}
\]

\[
\begin{array}{cccccccc}
J_{\text{ex}} & -33.9 & -44.1 & -33.9 & -44.1 & -33.9 & -44.1 \\
J_{\text{ex}} & +7.0 & -0.94 & +4.0 & +1.7 & +0.71 & +1.7 \\
\Delta_x & 8100 & 33 500 & 36 300 & 9470 & 30 600 & 30 600 \\
S & 0.17 & ~0 & 0.14 & 0.14 & ~0 & ~0 \\
\end{array}
\]

\( ^{\text{a}}\text{Sm-radical exchange coupling constant.} \ ^{\text{b}}\text{Sm--Sm exchange coupling constant.} \)
Although pathway is provided by a structure of the \[L_3\text{-edge XAS, where the homologous families of complexes have been examined by Sm}\]

The calculated exchange coupling constants are slightly smaller than for \[2\text{-S}_2\], a consequence of the larger \[\text{Sm}_2\text{S}_2\] core.

Dichalcogenide ligands can also be oxidized to the \((E_\text{I})^{-}\) redox level that is also paramagnetic. 17,18,19 The optimized structure of the \[2\text{-S}_2\] model gave a S–S bond distance of 2.149 Å, which is longer than observed experimentally for \[2\text{-S}_2\] but shorter than in the optimized neutral compound (Table S15). This is consistent with an increase in the bond order to form a supersulfide group. In contrast, optimization of the oxidized \[2\text{-Se}_2\] model failed to converge, highlighting the reluctance of Se to multiply bond with itself.5 The ligand-based SOMO is the \[\pi^*\] orbital, which antiferromagnetically couples to a metal-based SOMO of matching symmetry composed of the \(f_{\text{ync}}\) orbital of each Sm(III) ion (Figure 8). The overlap integral (S = 0.14) is marginally smaller than for the \[2\text{-S}_2\] model and suggests that the anticipated increase in overlap provided by the Se 4p orbitals is counteracted by the larger spatial separation of the paramagnetic centers. Hence, the \[S_2^\text{2+}\] ligand in \[2\text{-S}_2\] is more effective at penetrating the 4f orbitals because of its extra (negative) charge. This is best seen in the Mulliken spin population of \[2\text{-S}_2\] with more than five spins at each Sm ion but only ~0.88 spins on the bridging sulfur atoms, where the bond polarization shifts to the nitrogen donors of the \(N^\text{1+}\) ligand (Figure 8). The S–S \(\pi^*\) SOMO has only 68.4% 3p content, with a further reduction in the Sm 4f and 5d contribution compared with the \(\sigma^*\) SOMO (Table S21). However, it is much closer in energy to the 4f manifold, with a separation \(\Delta_\text{e} = 1400\text{ cm}^{-1}\) making the electron transfer process more facile. Despite the larger dimension, the calculated exchange constant of \(J_\text{ex} = -44.1\text{ cm}^{-1}\) is a third larger than that calculated for the \[2\text{-S}_2\] model (Table S5). This may suggest that a more efficient exchange pathway is provided by a \(\pi\) radical compared with a \(\sigma\) radical, although \(J_\text{ex}\) is half the size and a consequence of the larger intermetallic separation in \[2\text{-S}_2\]. Any electronic influence on this distortion exerted by the core atoms would be very small and easily overridden by the steric demands of the coligands and coordination environment of the Sm ion.

\section*{Conclusions}

The single-electron transfer chemistry of \([\text{Sm}(N^{1+})_2]\) has been utilized to produce a suite of mono- and dinuclear chalcogen complexes. This redox chemistry should be transferable to a wide range of Ln(II) and Ln(III) reduced dinitrogen complexes, and the nuclearity of the products can be easily tuned by subtle variations in ligand steric. These structurally homologous families of complexes have been examined by Sm \(L_3\)-edge XAS, where the fluorescence detection method provides well resolved pre-edge and white-line features. The straightforward TD-DFT protocol developed previously for Sm \(L_3\)-edge spectra was successfully used to reproduce the key spectral features. The experimentally validated protocol was applied to the calculation of the ground state electronic structure of models of \[2\text{-E}_2\]. One-electron oxidation and reduction of \[2\text{-S}_2\] is ligand-centered. Oxidation gave a bridging supersulfide in \[2\text{-S}_2\], and reduction gave a subsulfide in \[2\text{-S}_2\]. On the other hand, only the reduced \[2\text{-Se}_2\] species is calculated to be stable. The exchange interaction provided by these contrasting \(\sigma\)- and \(\pi\)-radical ligands was assessed by the magnitude of the calculated exchange coupling constants, which showed that the \(\pi\) SOMO in the supersulfide produced the strongest Sm–radical coupling, but the \(\sigma\) SOMO in the subsulfide gave the larger Sm–Sm exchange interaction. These \(J_\text{ex}\) values are roughly equivalent to those in benchmark \((N_2)_2^\text{2+}\) bridged species, but both \[2\text{-S}_2\] and \[2\text{-S}_2\] models gave superior \(J_\text{ex}\) values, highlighting the advantage of larger donor atoms. Therefore, dichalcogenides, in particular the radicals of disulfide, could be potential successors to their dinitrogen counterparts. Their application to chemical systems pertinent to molecular magnetism requires addressing an important design criterion, namely the coligand. Although the significant bulk of \(N^{1+}\) is advantageous in stabilizing exotic near-linear Ln(II) and bent Ln(III) species,\textsuperscript{24,25,30} its size hinders subsequent redox activation of the dichalcogenide bridging ligand. This impediment becomes more acute with the magnetically popular Ln ions with smaller ionic radii.\textsuperscript{8} This obstacle is circumvented by scaling the size of the coligand to match the \(f\)-element, where bis(silyl)amides present an almost linear approach.\textsuperscript{35,74} An alternative strategy is a shift to An, which not only eliminates the coligand dependency\textsuperscript{44} but the more diffuse \(5f\)-orbitals offers greater covalency and potentially stronger magnetic coupling.\textsuperscript{9} We anticipate that such studies could provide molecular magnets with monstrous exchange interactions, together with rich information on \(4f\) vs \(5f\) covalency.

\section*{Associated Content}

\section*{Supporting Information}

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00470.

Syntheses, crystallography, molecular structures of \(2\text{-S}_2\)-polymorph and 4–7, NMR spectroscopy, VT NMR spectroscopy, magnetometry, cyclic voltammetry, electronic spectroscopy, FTIR spectroscopy, X-ray absorption spectroscopy, and density functional theoretical calculations (PDF).

\section*{Accession Codes}

CCDC 1945230–1945240 contain the supplementary crystallographic information for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

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Notes
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