

# A Mesoionic Diselenolene Anion and the Corresponding Radical Dianion

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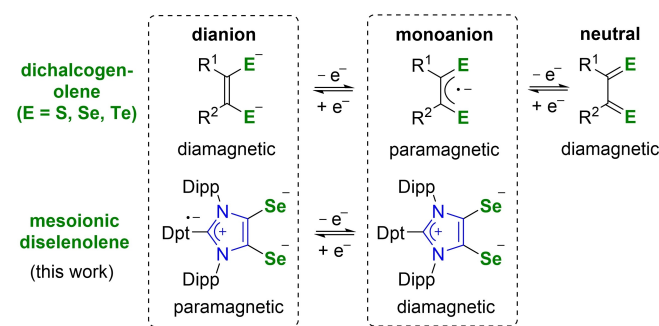
**Abstract:** Dichalcogenolenes are archetypal redox non-innocent ligands with numerous applications. Herein, a diselenolene ligand with fundamentally different electronic properties is described. A mesoionic diselenolene was prepared by selenation of a C2-protected imidazolium salt. This ligand is diamagnetic, which is in contrast to the paramagnetic nature of standard dichalcogenolene monoanions. The new ligand is

also redox-active, as demonstrated by isolation of a stable diselenolene radical dianion. The unique electronic properties of the new ligand give rise to unusual coordination chemistry. Thus, preparation of a hexacoordinate aluminum tris(diselenolene) complex and a Lewis acidic aluminate complex with two ligand-centered unpaired electrons was achieved.

## Introduction

Dichalcogenolenes are chelate ligands of the general formula  $R^1R^2C_2E_2$  ( $E = S, Se, Te$ ).<sup>[1]</sup> They can exist in three distinct redox states: a dianionic dichalcogenolate, a monoanionic dichalcogen radical, and a neutral dichalcogenone (Figure 1, top). Metal complexes with dichalcogenolene ligands can display unusual optical, electrochemical, magnetic, and structural properties, and considerable efforts have been made to understand the electronic structure of these compounds.<sup>[1,2]</sup> In parallel, potential applications have been explored. For example, dichalcogenolene complexes have been studied in the context of molecular (super)conductors,<sup>[3]</sup> nonlinear optics,<sup>[4]</sup> and photocatalysis.<sup>[5]</sup>

It is possible to alter the ligand properties of dichalcogenolenes by varying the donor atom (S, Se, or Te) and/or by modifying the ligand backbone. These approaches have been used extensively to fine-tune the donor characteristics and the redox properties of dichalcogenolene ligands.<sup>[1–5]</sup>



**Figure 1.** The three redox states of standard dichalcogenolene ligands and the mesoionic diselenolene ligands described herein (Dpt = 4,6-diphenyltriazinyl; Dipp = 2,6-diisopropylphenyl).

Below, we describe a diselenolene ligand with fundamentally different electronic properties. By double selenation of a C2-protected imidazolium salt, we have obtained a mesoionic diselenolene monoanion (Figure 1, bottom). The easy-to-access compound is diamagnetic, which is in contrast to the paramagnetic nature of standard dichalcogenolene monoanions.<sup>[1,2]</sup> Furthermore, we demonstrate that the monoanion can be reduced to give a stable radical dianion.<sup>[6,7]</sup> The unique electronic situation of the mesoionic diselenolene ligand gives rise to unusual coordination chemistry, as evidenced by the synthesis of penta- and hexa-coordinated Al(III) complexes, including a crystallographically characterized biradical.

## Results and Discussion

We recently reported that deprotonation of imidazolium salt **1** (Scheme 1) with a diphenyltriazinyl (Dpt) substituent at C2-position gave a  $\pi$ -acidic mesoionic carbene ligand.<sup>[8]</sup> In the course of our investigations, we found that **1** could be used as precursor to prepare the mesoionic diselenolene ligand **2**. The

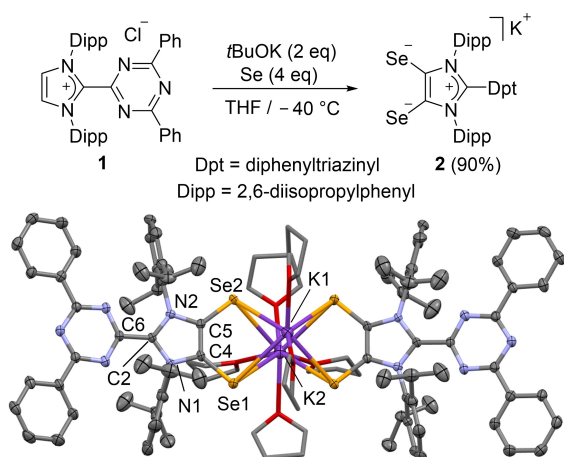
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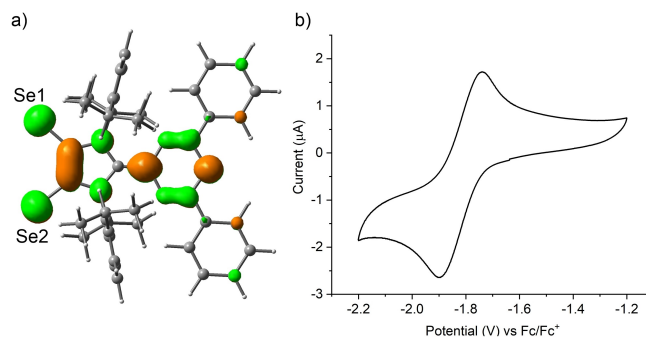
**Scheme 1.** Synthesis of the potassium salt **2** containing a diselenolene monoanion, and its molecular structure in the crystal (thermal ellipsoids at 50% probability, hydrogen atoms are omitted for clarity, THF molecules are simplified as wireframes).

reaction of two equivalents of potassium tert-butoxide (tBuOK) with imidazolium salt **1** in THF at  $-40^\circ\text{C}$ , followed by addition of excess elemental selenium,<sup>[9]</sup> resulted in the formation of **2**, which could be isolated in the form of a purple solid in 90% yield (Scheme 1).

The structure of **2** in the solid state was established by single crystal X-ray diffraction (XRD) analysis (Scheme 1).<sup>[10]</sup> Two symmetry-related diselenolene ligands are linked together by coordination to two potassium ions ( $d(\text{K}\cdots\text{Se})=3.382(6)\text{--}3.521(7)\text{ \AA}$ ) (Figure S15). The coordination environment around the hexa-coordinated K1 ion can be described as trigonal prismatic, with the remaining sites being occupied by two THF ligands. The K2 ion, on the other hand, is octa-coordinated, with four additional THF ligands. The Se–C bonds (1.850(4) and 1.852(4) Å) are shorter than what was found for metal complexes with benzene-1,2-diselenolato ligands ( $\sim 1.91\text{ \AA}$ ),<sup>[11]</sup> and the C4–C5 bond length (1.419(4) Å) is in between that of standard C–C single and C=C double bonds (Table S3).<sup>[12]</sup> These structural data reflect the mesoionic character of the ligand, and they indicate that the  $\text{C}_2\text{Se}_2$  unit of **2** is distinct from that of a dianionic diselenolate group. The co-planar arrangement of the triazinyl-, the phenyl-, and the imidazole rings implies extended  $\pi$ -conjugation.

In order to gain further insight into the electronic structure of **2**, density-functional theory (DFT) calculations were performed at B3LYP-D3(BJ)/def2-SVP level.<sup>[13]</sup> The calculated structures are very close to those determined by XRD analyses. The highest occupied molecular orbitals (HOMO to HOMO-3) of **2** are mainly composed of the p-orbitals at Se (Figure S25). The lowest unoccupied molecular orbital (LUMO) predominantly involves  $\pi$ -antibonding orbitals (Figure 2a), suggesting that it might be possible to reduce the ligand.

Cyclic voltammetry (CV) revealed a reversible one-electron reduction at  $E_{1/2} = -1.80\text{ V}$ , referenced to an external ferrocene/ferrocene redox couple (Figure 2b). The reduction poten-

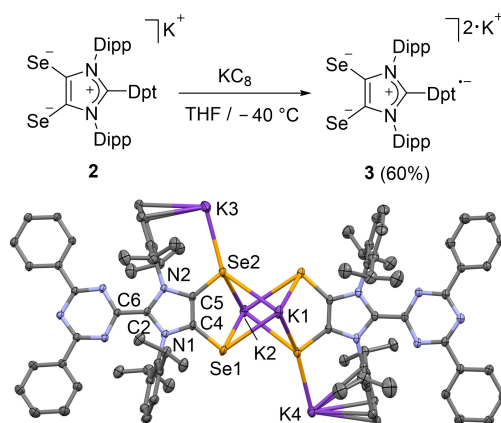


**Figure 2.** a) Surface diagram of the LUMO of **2** (isovalue = 0.04; calculated at the B3LYP-D3(BJ)/def2-SVP level). b) Cyclic voltammogram of **2** at  $0.1\text{ V s}^{-1}$  scan rate in THF /  $0.1\text{ M [nBu}_4\text{N][PF}_6\text{]}$ .

tial is within the expected range for substituted imidazolium salts ( $-1.4$  to  $-2.1\text{ V}$ ).<sup>[14]</sup>

On a preparative scale, reduction of the **2** was accomplished by using one equivalent of potassium graphite in THF at  $-40^\circ\text{C}$ . Upon addition of  $\text{KC}_8$ , the color of the solution changed immediately to dark purple. After workup, compound **3** was isolated as a purple solid in 60% yield (Scheme 2). The product was NMR-silent and EPR-active, indicating the formation of a paramagnetic compound (Figure S2c). HRMS and single crystal XRD analyses confirmed that a potassium salt of a diselenolene radical dianion, **3**, had formed (Scheme 2). In line with the purple color, the UV/Vis spectrum (THF) showed a broad absorption band at  $\lambda = 601\text{ nm}$  (Figure S2a). In solution, **3** was found to decompose slowly when stored under a dinitrogen atmosphere at room temperature (Figure S2b).

Crystals of **3** were obtained from THF/Et<sub>2</sub>O (1:1) at room temperature, and a single crystal XRD analysis was performed. In the solid state, eight independent diselenolene units are connected through potassium-selenium interactions and flanking potassium-arene contacts (Scheme 2 and Figure S16). The bond lengths of the diselenolene dianions are all very similar.

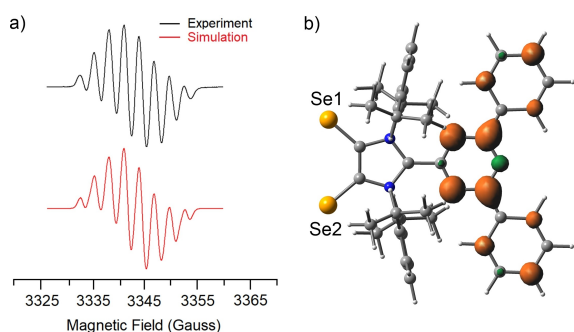


**Scheme 2.** Synthesis of the potassium salt **3** containing a diselenolene radical dianion, and its molecular structure in the crystal (only two of the eight independent diselenolene dianions are shown, thermal ellipsoids at 50% probability, hydrogen atoms are omitted for clarity).

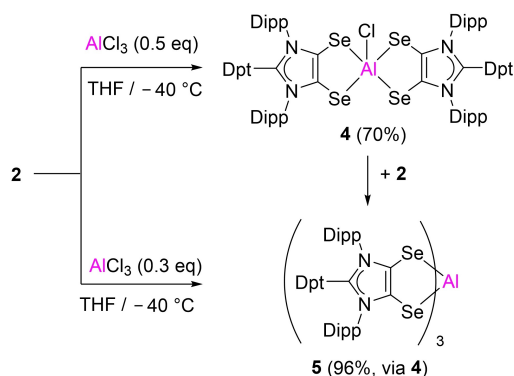
Compared to the diselenolene monoanion in **2**, slightly longer Se–C bonds (av. = 1.882 Å) and shorter C4–C5 bonds (av. = 1.365 Å) are observed (Table S3). As found for **2**, the imidazole heterocycle and the rings of the Dpt group are almost coplanar. The C2–C6 bonds in **3** (av. = 1.413 Å) are slightly shorter than the C2–C6 bond in **2** (1.453(18) Å). In contrast to the nearly equidistant C–N bonds of the triazinyl rings in **1** and **2**, a slight bond-length alternation is observed for the C<sub>3</sub>N<sub>3</sub> ring in **3** (Table S3).<sup>[6]</sup>

The radical **3** was also characterized by X-band electron paramagnetic resonance (EPR) spectroscopy (Figure 3a). The room temperature EPR spectrum of **3** in THF features a singlet with hyperfine splitting due to coupling to two equivalent <sup>14</sup>N<sub>3,5</sub> nuclei, one <sup>14</sup>N<sub>4</sub> nucleus, and two sets of equivalent <sup>1</sup>H nuclei, i.e. two <sup>1</sup>H<sub>p-ph</sub> and four <sup>1</sup>H<sub>o-ph</sub> nuclei. The spectrum can be simulated by using the following parameters:  $g = 2.0041$ ,  $A(^{14}\text{N}_{3,5}) = 3.35$  G,  $A(^{14}\text{N}_4) = 1.45$  G,  $A(^1\text{H}_{p-ph}) = 2.57$  G,  $A(^1\text{H}_{o-ph}) = 0.25$  G (for details, see the Supporting Information). The EPR data indicate that the unpaired electron is delocalized over the peripheral  $\pi$ -conjugated diphenyltriazinyl group.

The electronic structure of the radical dianion **3** was analyzed by DFT calculations at the UB3LYP-D3(BJ)/def2-SVP level of theory.<sup>[13]</sup> The calculated spin density of the unpaired electron is mainly distributed over the peripheral  $\pi$ -conjugated Dpt substituent (Figure 3b). This result is in line with the EPR



**Figure 3.** a) Experimental (THF, 290 K) and simulated EPR spectra of the diselenolene radical dianion **3**. b) Calculated spin density of the unpaired electron (isovalue = 0.003; calculated at the UB3LYP-D3(BJ)/def2-SVP level).



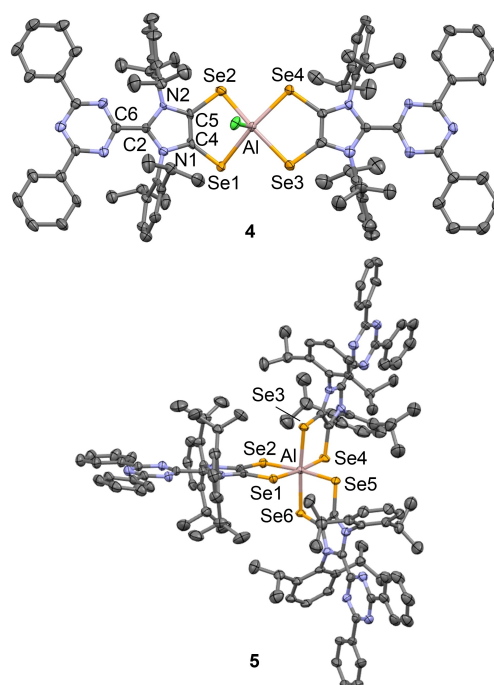
**Scheme 3.** Synthesis of the neutral aluminum bis(diselenolene) and tris(diselenolene) complexes **4** and **5**.

data. It is worth noting that the distribution of electron density in **3** is distinct from other imidazole-based radicals, for which significant spin density is usually found on the imidazole ring.<sup>[14]</sup>

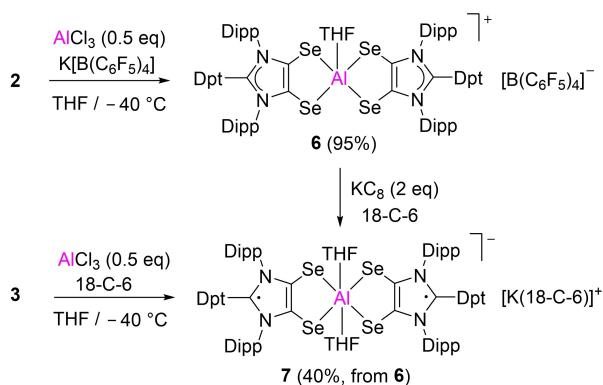
The coordination chemistry of dichalcogenolene ligands and aluminum is largely unexplored,<sup>[15]</sup> and we are interested whether diselenolene **2** could be used as ligand for this metal. First, we examined the reactivity of **2** towards anhydrous AlCl<sub>3</sub>. When one equivalent of AlCl<sub>3</sub> was added to a THF solution of two equivalents of **2** at –40 °C, the neutral chloroaluminum bis(diselenolene) complex **4** was formed in 70% yield (Scheme 3). Complex **4** could further react with **2**, giving the neutral aluminum tris(diselenolene) complex **5** in a yield of 96% (Scheme 3). A direct one-pot synthesis of **5** was achieved by adding 0.3 equivalents of AlCl<sub>3</sub> to **2** in THF (yield: 85%). The aluminum complexes **4** and **5** were characterized by NMR spectroscopy, as well as by single crystal XRD analyses.

Graphic representations of the solid-state structures of **4** and **5** are depicted in Figure 4. The penta-coordinate aluminum in **4** adopts a square pyramidal coordination environment. The Se–Al bond lengths in **4** (av. 2.50 Å) are within the range reported for other Al(III) selenato complexes.<sup>[16]</sup> The Se–Al bonds (av. 2.55 Å) in **5** are slightly longer than those of **4**. The hexa-coordinate Al in **5** shows in nearly ideal octahedral coordination environment, with a trigonal twist angle of  $\phi = 59.7^\circ$  (Figure S20).<sup>[17]</sup> To the best of our knowledge, **4** and **5** represent the first aluminum complexes with a diselenolene ligand.

The cationic bis(diselenolene) complex **6** was synthesized by combining **2** with 0.5 equivalents of AlCl<sub>3</sub>, followed by addition of K[(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (Scheme 4). Alternatively, **6** was obtained



**Figure 4.** Molecular structures of the complexes **4** and **5** in the crystal (thermal ellipsoids at 50% probability, hydrogen atoms are omitted for clarity).



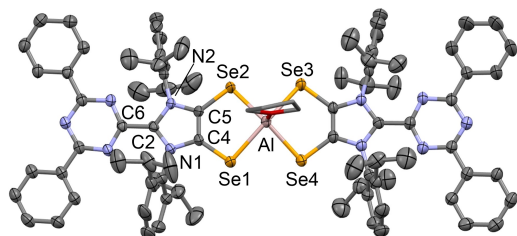
**Scheme 4.** Synthesis of the cationic bis(diselenolene) complex **6** and the anionic, paramagnetic bis(diselenolene) complex **7**.

by a salt metathesis reaction of **4** with  $\text{K}[\text{B}(\text{C}_6\text{F}_5)_4]$  in THF at room temperature (Scheme S5).

The solid-state structure of **6** shows a penta-coordinate aluminum with a square pyramidal geometry, similar to what was observed for **4** (Figure 5). The average Se–Al bond length in **6** is 2.49 Å, which is shorter than what was found for **4** and **5**. The Al–O bond length of 1.906(3) Å suggests strong binding of the THF ligand. In line with the structural data, the calculated bond dissociation energy (BDE) for the THF ligand is high ( $\text{BDE}(\text{Al}-\text{O}) = 180 \text{ kJ mol}^{-1}$ ).

The Lewis acidity of **6** was assessed using the Gutmann-Beckett NMR method.<sup>[18]</sup> One equivalent of  $\text{Et}_3\text{PO}$  was added to a solution of **6** in  $\text{CD}_2\text{Cl}_2$ , and a  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum was recorded. The resulting  $\text{OPEt}_3$  adduct displayed a sharp resonance at  $\delta = 74.8$  ppm, which corresponds to a shift of  $\Delta\delta = 24$  ppm compared to the value of free  $\text{Et}_3\text{PO}$  ( $\delta = 50.5$  ppm) (Figure S6). Accordingly, the Lewis acidity of **6** is comparable to that of  $\text{B}(\text{C}_6\text{F}_5)_3$  ( $\Delta\delta = 26$  ppm,  $\text{CDCl}_3$ )<sup>[18a]</sup> and  $\text{AlCl}_3$  ( $\Delta\delta = 28$  ppm,  $\text{CD}_2\text{Cl}_2$ ).<sup>[19]</sup>

Diradicals are even-electron compounds with two, possibly delocalized, radical centers.<sup>[20]</sup> These compounds have received considerable attention, both from a fundamental as well as from an application point-of-view.<sup>[21]</sup> Most diradicals are highly reactive and short-lived, and stable diradicals represent important synthetic targets. The redox-activity of the diselenolene ligand **2** prompted us to explore if we could achieve a two-fold reduction of the bis(diselenolene) complex **6**.<sup>[22]</sup> Indeed, a stable

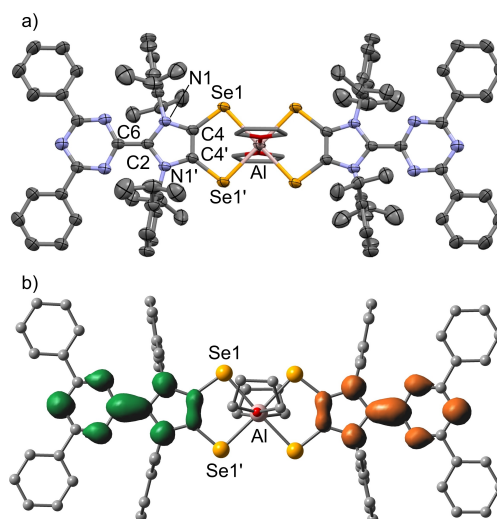


**Figure 5.** a) Molecular structure of complex **6** in the crystal (thermal ellipsoids at 50% probability, hydrogen atoms and the  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$  anion are omitted for clarity).

diradical, **7**, was obtained by reducing **6** with 2 equivalents of  $\text{KC}_8$  in the presence of 18-crown-6 (Scheme 4). Complex **7** could also be obtained by reaction of the reduced ligand **3** with  $\text{AlCl}_3$  (Scheme 4). THF solutions of **7** are moderately air sensitive, but they are stable when kept under inert atmosphere (Figure S7b).

The molecular structure of **7** in the crystal is depicted in Figure 6a. One can observe a hexa-coordinate aluminum with two diselenolene ligands and two THF ligands. The coordination of THF to the negatively charged bis(diselenolene) complex is noteworthy, because aluminate complexes are typically not Lewis acidic. A notable exception is a calix[4]pyrrole aluminate complex described by Greb and co-workers, which displays an unusual square planar geometry.<sup>[19]</sup> The Se–Al bond lengths are equidistant (2.513(3) Å) and similar as what was found for **6** (Table S3). The C2–C6 bond in **7** (1.402(6) Å) is significantly shorter than those of **4** (1.490(13) Å) and **6** (1.474(2) Å), implying a significant double bond character. Unlike the nearly equidistant C–N bonds of the triazinyl groups in **4–6**, a pronounced bond-length alternation is observed for the triazine ring in **7** (for details, see the Supporting Information).

Complex **7** was found to be NMR-silent, in line with its paramagnetic character. The room temperature EPR spectrum of **7** in THF corresponds to a singlet with hyperfine splitting from three types of  $^{14}\text{N}$  nuclei ( $A(^{14}\text{N}_a) = 3.58$  G,  $A(^{14}\text{N}_{1,2}) = 3.02$  G,  $A(^{14}\text{N}_{3,5}) = 0.45$  G) (Figure S12). The  $g$ -factor value for **7** is 2.0032. The results suggest that the two unpaired electrons in **7** are practically independent.<sup>[23]</sup> The presence of largely independent radical centers was also supported by variable temperature EPR (VT-EPR) measurements (for details, see Figure S14). In the temperature range from 20 to 100 K, the results could be fitted by applying the Curie model. At lower temperatures ( $T < 20$  K), a clear deviation from the Curie model towards antiferromagnetic coupling could be observed. These results lead to the conclusion that the singlet and triplet states in **7** are nearly



**Figure 6.** a) Molecular structure of complex **7** (thermal ellipsoids at 50% probability, hydrogen atoms and  $\text{K}^+$  [18-C-6] unit are omitted for clarity), and b) Calculated spin density of the open-shell singlet ground state of **7** ( $\alpha$ -spin: green;  $\beta$ -spin: orange; isovalue = 0.003; calculated at the UB3LYP-D3(BJ)/def2-SVP level).

isoenergetic. Therefore, the corresponding  $J$ -coupling constant (the Bleaney-Bowers approach)<sup>[24]</sup> is very small.

The electronic structure of **7** was further elucidated by computational chemistry. The open-shell singlet and triplet states were found to be nearly isoenergetic, but more stable than the closed-shell state by 59 kJ mol<sup>-1</sup> (Table S5). The calculated spin density for biradical **7** reveals that the  $\alpha$ - and  $\beta$ -spins are identically distributed over the imidazole and triazinyl heterocycles (Figure 6b).

## Conclusion

A diselenolene ligand was prepared by selenation of a C2-protected imidazolium salt. The ligand has two distinct features: a) it is mesoionic and displays an overall charge of minus one, and b) it can be reduced to give a stable dianionic radical. These features distinguish the new ligand from standard dichalcogenolenes, where the dianionic form is diamagnetic and the monoanionic form is paramagnetic. The presence of the Dpt substituent is a crucial design element, because its electron-withdrawing nature is expected to facilitate the reduction to the radical state.<sup>[6]</sup> The importance of the Dpt substituent is substantiated by the fact that the spin density of the radical dianion is largely localized on this group.

To demonstrate the utility of the new ligand, we have prepared aluminum bis- and tris(diselenolene) complexes. To the best of our knowledge, these complexes represent the first dichalcogenolene complexes of Al(III). The redox activity of the ligand is maintained when coordinated to aluminum, as evidenced by synthesis of an aluminum bis(diselenolene) biradical anion. Notably, the aluminate complex is still Lewis acidic, with two additional THF ligands bound to Al. These first results show that mesoionic dichalcogenolene ligands such as **2** can give rise to unusual coordination chemistry.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** aluminum complex · biradical · diselenolene · electronic structure · radical · X-ray diffraction

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