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Redox chemistry of an anionic dithiolene radical†

Yuzhong Wang, Yaoming Xie, Pingrong Wei, Henry F. Schaefer, III and Gregory H. Robinson *

The redox chemistry of the first stable anionic dithiolene radical 1$^{\bullet}$ was investigated by both reactivity and cyclic voltammetry studies. While one-electron reduction of 1$^{\bullet}$ by Cp_2Co or KC_8 affords the corresponding dithiolate dimers 2 and 3, respectively, one-electron oxidation of 1$^{\bullet}$ by $Ph_3C^+BF_4^-$ (or O_2) conveniently gives 4, the neutral dithiolene dimer.

Largely due to unusual optical, conductive, magnetic, and bio-inspired properties, studies of transition metal dithiolene complexes may be traced to the 1960s.[1–13] While molybdenum– and tungsten–dithiolene complexes have shown enzymatic activity,[2,5,12] other transition metal bis-dithiolenes have demonstrated remarkable potential as optoelectronic materials.[4,7,10,11] The non-innocent nature of dithiolene ligands (Fig. 1) plays a pivotal role in the intriguing redox chemistry of transition metal dithiolenes.[3]

While the radical character of dithiolene ligands ($L^{\bullet-}$) in transition metal complexes was well documented,[8,15–27] highly reactive transition metal-free anionic dithiolene radicals have only been investigated using theoretical methods and electron paramagnetic resonance.[28–31] Notably, the electronic absorption spectrum of the prototype anionic dithiolene radical ($C_2H_2S_2^{\bullet-}$) was studied in a low-temperature matrix.[32] Recently, the first structurally characterized anionic dithiolene radical **1**$^{\bullet}$ was synthesized by this laboratory *via* trisulfurization of the corresponding anionic N-heterocyclic dicarbene[33] (Scheme 1).[34] It was anticipated that this discovery could provide a unique platform for accessing the largely unexplored chemistry of main group dithiolene radicals (*e.g.*, boron dithiolene radicals were achieved *via* **1**$^{\bullet}$).[35] Moreover, the considerable stability of **1**$^{\bullet}$ could be advantageous for probing the redox chemistry of dithiolene radical anions ($L^{\bullet-}$ in Fig. 1). To this end, we report the syntheses,[36] molecular structures[36] and computations[36] of compounds **2**, **3**, and **4**, all obtained *via* one-electron redox reactions of **1**$^{\bullet}$.

The cyclic voltammogram of **1**$^{\bullet}$ was recorded in THF (Fig. 2), potentials are reported *versus* an internal ferrocene/ferrocenium (Fc/Fc^+) standard. While both reversible and quasi-reversible redox events have been documented for transition metal dithiolene complexes,[37,38] radical **1**$^{\bullet}$ exhibits two electrochemically quasi-reversible, diffusion-controlled couples at $E_{1/2} = -0.78$ V ($\Delta E_p = 0.21$ V) and $E_{1/2} = -1.47$ V ($\Delta E_p = 0.25$ V), which are assigned to [$L^0/L^{\bullet-}$] and [$L^{\bullet-}/L^{2-}$] ligand reduction events, respectively. Indeed, with increasing scan rate (Fig. S1†),[36] the cathodic-anodic peak separations (ΔE_p) increase and meanwhile cathodic peak potentials (E_{pc}) shift negatively. The one-electron reduction/oxidation of **1**$^{\bullet}$ involves adding/removing one electron from the SOMO,[2] which is comparable to that for neutral odd-electron 1,2-dithioles.[39] The small irreversible reduction at −1.13 V may be a result of certain chemical transformations, such as radical coupling to yield dithiete or dimer of L^0. The 1 : 1 reaction of **1**$^{\bullet}$ with cobaltocene (Cp_2Co), a well known one-electron reducing agent,[40] quantitatively affords dimeric dithiolate **2** (as a green powder) (Scheme 2). Compound **2** is insoluble in toluene, slightly soluble in THF, and moderately soluble in acetonitrile. Although turquoise-coloured X-ray quality crystals of **2** were obtained from acetonitrile, the significantly broadening of the ^1H NMR spectrum pattern of **2** in CD_3CN and THF-d_8 suggests the partial dissociation of **2**. Consequently, ideal NMR data of **2** could not be obtained in polar solvents. In addition, potassium graphite (KC_8) reduction of **1**$^{\bullet}$ in THF quantitatively provided the lithium-potassium mixed alkali metal dithiolate

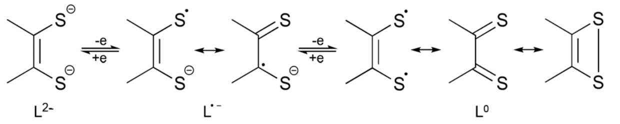

Fig. 1 Redox non-innocence of a dithiolene ligand.[14]

Department of Chemistry, The University of Georgia, Athens, Georgia 30602-2556, USA. E-mail: robinson@uga.edu

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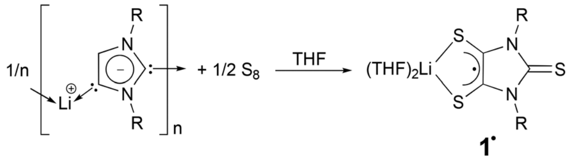


Scheme 1 Previously reported synthesis of $\mathbf{1}^{\bullet}$ (R = 2,6-diisopropylphenyl).[34]

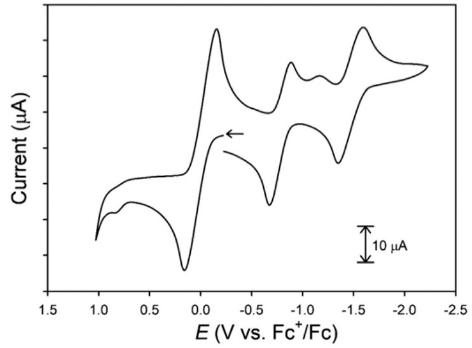
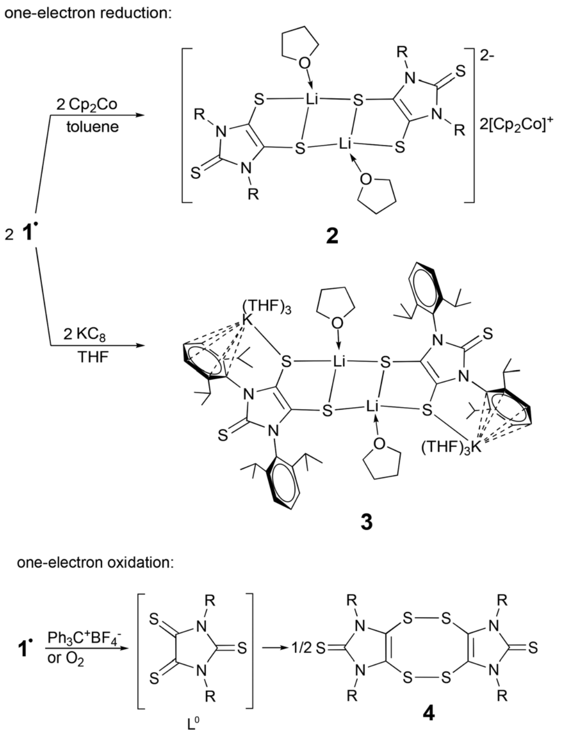


Fig. 2 Cyclic voltammogram of $\mathbf{1}^{\bullet}$ (6.45 mM) with Fc internal standard (4.5 mM; $E_{1/2}$ set to 0 V) in THF (scan speed: 100 mV s^{-1}, 0.1 M $^{n}Bu_4NPF_6$ supporting electrolyte, glassy carbon working electrode, Pt-wire counter electrode, RT). Arrow indicates direction of the scan.

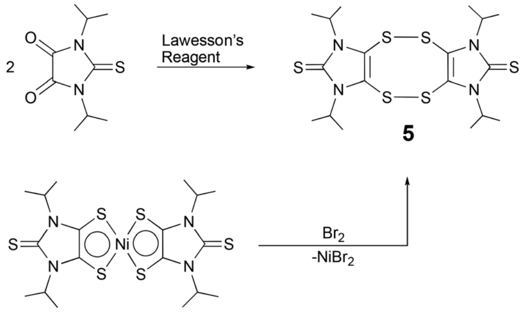


Scheme 2 Synthesis of compounds **2**, **3**, and **4** (R = 2,6-diisopropylphenyl).

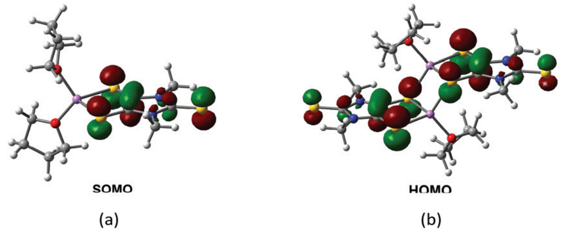
dimer **3** (Scheme 2). However, the presence of trace amounts of O_2 result in the oxidation of **3**, yielding unidentified products with the colour change from colourless to purple.

Reaction of $\mathbf{1}^{\bullet}$ with $Ph_3C^+BF_4^-$ (in a 1 : 1 ratio) in toluene leads to one-electron oxidation of $\mathbf{1}^{\bullet}$,[40] giving orange-red crystals of **4** (a dimer of the neutral dithiolene ligand; L^0 in Fig. 1) in 55.3% yield (Scheme 2). Alternatively, **4** may also be obtained by dioxygen oxidation of $\mathbf{1}^{\bullet}$. Notably, compound **5**, the analogue of **4**, has been synthesized as previously reported *via* two unique routes (Scheme 3): (1) sulfurization of imidazole-based dione with Lawesson's reagent;[41,42] and (2) oxidation of the nickel bis-dithiolene complex by Br_2.[41,43] Compounds **4** and **5** may serve as convenient platforms to access metal dithiolene complexes *via* reductive cleavage of the S–S bonds.[43]

X-ray structural analysis[36] of **2** (Fig. 4) shows that the $[\mathbf{2}]^{2-}$ moieties contain two lithium dithiolene units dimerized through two Li–S bonds. With THF-coordination, each lithium atom is four-coordinate and adopts a distorted tetrahedral geometry. The central Li_2S_2 ring is planar, in which the bridging Li–S bond [2.396(15) Å] is *ca.* 0.13 Å shorter than those in the neighbouring LiS_2C_2 ring [2.525(16) Å]. The LiS_2C_2 rings in **2** are somewhat more bent than that in $\mathbf{1}^{\bullet}$ [the bend angle (η) between the LiS_2 plane and the S_2C_2 plane = 17.6° for **2** *vs.* 14.2° for $\mathbf{1}^{\bullet}$].[34] By comparison with $\mathbf{1}^{\bullet}$ [d_{C-C} = 1.417(3) Å; d_{C-S} = 1.677(3) Å, av],[34] compound **2** exhibits shorter olefinic C–C bonds [1.362(8) Å] and concomitant longer C–S bonds [1.729(8) Å, av]. These distances compare well to those for the free dithiolate ligand $(NMe_4)_2(C_3S_5)$[44] [d_{C-C} = 1.371(8) Å; d_{C-S} = 1.724(6) Å] and the theoretical values for the simplified $[\mathbf{2\text{-}Me}]^{2-}$ model (d_{C-C} = 1.375 Å; d_{C-S} = 1.754 Å).[36] The ligand-based HOMO of dimeric dithiolate $[\mathbf{2\text{-}Me}]^{2-}$ (Fig. 3b) mainly involves C–C π-bonding and C–S π-antibonding character, which is relevant to the SOMO of its radical precursor $[\mathbf{1\text{-}Me}]^{\bullet}$ [36] (Fig. 3a) and consistent with the C–C and C–S bond



Scheme 3 Previously reported synthetic routes of **5**.[41–43]



(a) (b)

Fig. 3 Selected molecular orbitals of the simplified models $[\mathbf{1\text{-}Me}]^{\bullet}$ (a) and $[\mathbf{2\text{-}Me}]^{2-}$ (b).

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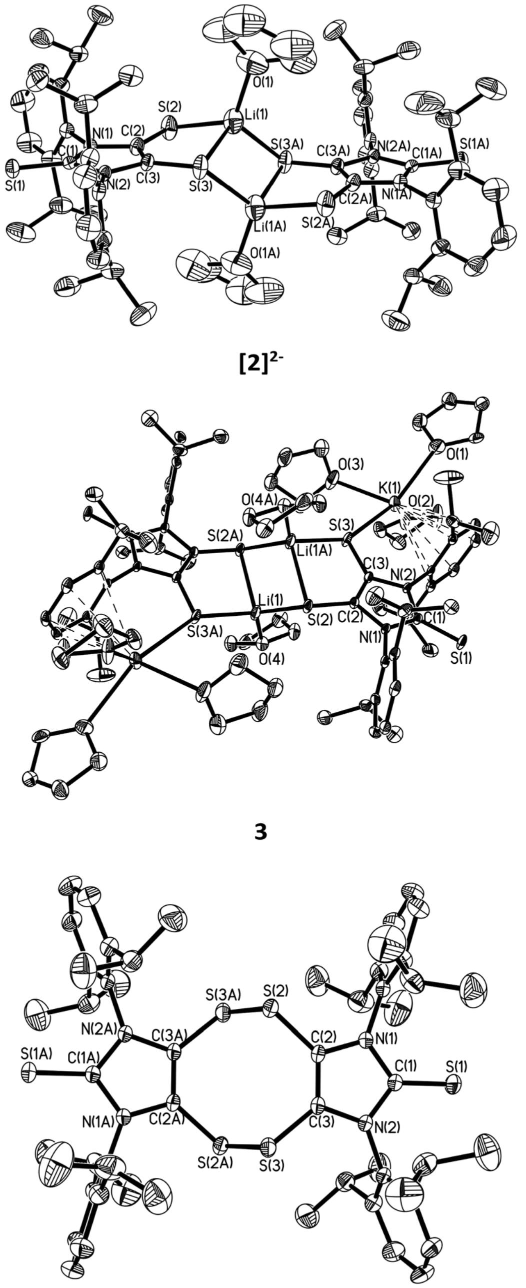

$[\mathbf{2}]^{2-}$

3

4

Fig. 4 Molecular structures of $[\mathbf{2}]^{2-}$, **3**, and **4**. Thermal ellipsoids represent 30% probability: hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) are as follows. For $[\mathbf{2}]^{2-}$, C(1)–S(1) 1.680(6), C(2)–C(3) 1.362(8), C(2)–S(2) 1.724(6), C(3)–S(3) 1.733(6), S(2)–Li(1) 2.434(15), S(3)–Li(1) 2.525(16), S(3A)–Li(1) 2.396(15), O(1)–Li(1) 1.961(18); S(2)–C(2)–C(3) 131.1(5), C(2)–S(2)–Li(1) 92.0(4), S(2)–Li(1)–S(3) 93.6(5), S(3)–Li(1)–S(3A) 111.7(7), O(1)–Li(1)–S(2) 120.5(8). For **3**, C(1)–S(1) 1.701(3), C(2)–C(3) 1.366(5), C(2)–S(2) 1.733(3), C(3)–S(3) 1.732(4), S(2)–Li(1) 2.416(8), S(2)–Li(1A) 2.531(7), S(3)–Li(1A) 2.407(7), S(3)–K(1) 3.1490(13), O(4)–Li(1) 1.960(9); S(2)–C(2)–C(3) 130.7(3), C(2)–S(2)–Li(1A) 90.09(19), S(2)–Li(1A)–S(3) 94.2(2), S(2)–Li(1A)–S(2A) 110.8(3), C(3)–S(3)–K(1) 115.01(12). For **4**, C(1)–S(1) 1.655(2), C(2)–C(3) 1.348(3), C(2)–S(2) 1.739(2), C(3)–S(3) 1.739(2), S(3)–S(2A) 2.0728(9); S(2)–C(2)–C(3) 129.74(17), C(2)–S(2)–S(3A) 104.28(8).

distance change of the C_2S_2 units in **2** in comparison with those for $\mathbf{1}^{\bullet}$.[34] Similar to that in $[\mathbf{1\text{-}Ph}]^{\bullet}$,[34] the LiS_2C_2 rings in $[\mathbf{1\text{-}Me}]^{\bullet}$ and $[\mathbf{2\text{-}Me}]^{2-}$ are nearly planar in the gas phase.

Compound **3** is a Li–K mixed metal dithiolate dimer in the solid state.[36] The central $[C_2S_2Li(THF)]_2$ core in **3** shows similar geometry and bonding parameters to that in **2** (see the caption of Fig. 4). The potassium cation in **3** is σ-bonded to a sulphur atom and coordinated to three THF molecules. The potassium-phenyl centroid distance (2.990 Å) in **3** compares well with that [3.034(9) Å] in $[\{K\{(2,6\text{-}iPr_2C_6H_3N)_2CH\}_2K(THF)_2\}_n]\cdot n$THF,[45] which suggests the presence of cation–π interaction between the potassium cation and the phenyl ring.[46] The S–K bond distance for **3** [3.1490(13) Å] is comparable to that in $[\{Ce(Cp^*)_2(dddt)K(thf)_2\}_2]$ (dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate)[47] [3.26(5) Å] and in the simplified model **3-Ph** (3.210 Å).[36] The Wiberg bond indices of the K–S bonds in **3-Ph** are 0.11, suggesting their strong ionic character. In the solid state,[36] the central eight-membered C_4S_4 ring of **4** (Fig. 4) adopts a chair conformation as suggested by torsion angles [*i.e.*, C(2)–S(2)–S(3A)–C(3A), 97.81°; C(2)–C(3)–S(3)–S(2A), 75.50°], which are similar to those reported for **5** [C–S–S–C, 101.8(6)°; S–S–C–C, −82(1) and 79(1)°].[42] The C–C bonds [1.348(3) Å] and C–S bonds [1.739(2) Å] in the C_2S_2 units of **4** are also similar to those in **5** [$d_{C\text{–}C}$ = 1.36(2) Å; $d_{C\text{–}S}$ = 1.75(1) Å, av].[42] The S–S bond in **4** [2.0728(9) Å] is a typical single bond, involving predominant 3p character (92.50%).[36]

Conclusions

While reactions of stable lithium dithiolene radical $\mathbf{1}^{\bullet}$ with Cp_2Co or KC_8 give the corresponding one-electron reduction product **2** and **3**, respectively, combination of $\mathbf{1}^{\bullet}$ with $Ph_3C^+BF_4^-$ (or O_2), *via* one-electron oxidation, leads to the isolation of **4**. Further application of these neutral (**4**), mono-anionic ($\mathbf{1}^{\bullet}$), and dianionic (**3**) dithiolene species in main group chemistry is being investigated in this laboratory.

Conflicts of interest

There are no conflicts to declare.

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