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1,3-Thiazoline-2-thione-4,5-dithiolato, an efficient building block towards functionalized dithiadiazafulvalenes

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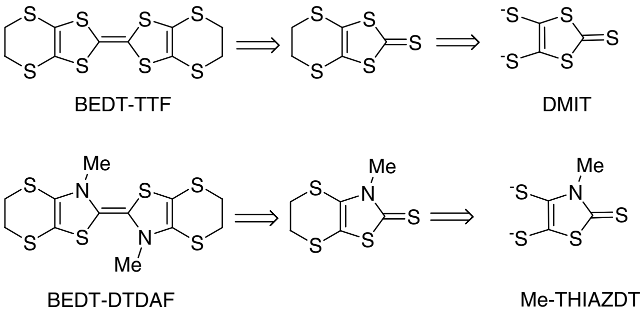
Abstract—The first synthesis and X-ray structural determination of the bis(tetraethylammonium) Zn dithiolene complex involving *N*-methyl-1,3-thiazoline-2-thione-4,5-dithiolate, $[NEt_4]_2[Zn(Me\text{-}thiazdt)_2]$, are reported. The reactivity of this dithiolene complex as a nucleophilic dithiolate synthon and as a precursor of the air sensitive electron rich olefine, the bis ethylenedithiodithiadiazafulvalene (BEDT–DTDAF), is also described.

In the field of molecular conductors, among the various synthesized tetrathiafulvalenes (TTF), the bis(ethylenedithio)tetrathiafulvalene (BEDT–TTF) is the one which has given rise to the largest variety of radical-ion salts exhibiting superconducting behaviour.[1] As a consequence, an enormous amount of research has been devoted to the synthesis, electrical properties and optical properties of BEDT–TTF analogues.[2] Ethylenedithio moieties play indeed a crucial role in the observed properties due to their specific supramolecular organization in the solid state.[3] Dithiadiazafulvalenes derivatives (DTDAFs), with their strong electron donating properties, constitute another interesting family as precursors of molecular materials.[4] Among the various DTDAF prepared so far, none of them bear the 'magic ethylenedithio' substituents. Therefore, in order to synthesize BEDT–DTDAF, we investigated first the synthesis of 1,3-thiazoline-2-thione-4,5-dithiolate, as it is known that its sulfur analogue 1,3-dithiole-2-thione-4,5-dithiolate (dmit) has been successfully used as a precursor of BEDT–TTF.[5] Herein, we wish to present an easy route to reach 1,3-thiazoline-2-thione-4,5-dithiolate (thiazdt) which is isolated as its zinc dithiolene complex. The structural and electrochemical properties of this complex are presented together with the synthetic strategy we used to reach BEDT–DTDAF.



Two main routes have been used for the synthesis of 1,3-dithiole-2-thione-4,5-dithiolate (dmit).[5] The most employed one is the DMF-mediated reduction of carbon disulfide by alkali metals where the dmit is easily isolated as the tetraethylammonium salt of its zinc chelate. Another alternative route consists in the lithiation of the 1,3-dithiole-2-thione followed by the in situ sulfur insertion into carbon–lithium bound. In a previous work on thiazole-2-thione derivatives, we have shown that it was possible to use this strategy towards monofunctionalization of the thiazole core.[6] Therefore, in view of the synthesis of the target molecule, we studied the bimetallation of the 1,3-thiazoline-2-thione core **1**. Actually, we found that the best way is a step by step lithiation and addition of sulfur. The methodology we used involves first the monometallation of the thiazole core using lithium diisopropylamide (LDA) followed by the addition of sulfur and subsequently metallation of the second position with LDA and addition of sulfur. This was realized by treating **1**[7] at −10 °C in THF with 1.5 equiv of

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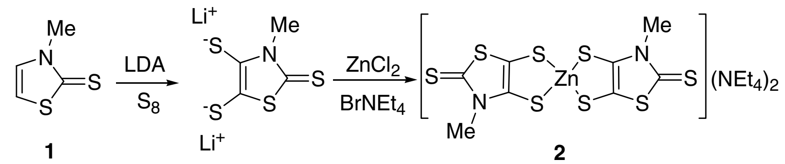


Scheme 1.

LDA and 1.5 equiv of sulfur for each step (Scheme 1). The dithiolate can behave as a ligand towards a metal atom such as Zinc(II). Therefore $ZnCl_2$ was added to the medium followed by the addition of tetraethyl ammonium bromide. This strategy allowed us to isolate complex **2**,[8] $[NEt_4]_2[Zn(Me\text{-}thiazdt)_2]$ in 64% yield, easily isolated from the other salts formed in the medium. It is noteworthy that recently Arca and co-workers reported the synthesis of neutral dithiolene complexes involving *N*-ethyl-1,3-thiazoline-2-thione-4,5-dithiolate $M(Et\text{-}thiazdt)_2$ (Ni, Pt) through the sulfuration of *N*-ethyl-2-thioxothiazolidine-4,5-dione with Lawesson's reagent in the presence of the metal or its ion.[9] Compared with this strategy which afforded the neutral dithiolene complexes in rather low yields (15% for Ni and 18% for Pt), the synthetic pathway described here allows us to isolate the dithiolene complex in higher yields. Note that only another example of a metal dithiolene complex involving 1,3-thiazoline-2-thione-4,5-dithiolate (R-thiazdt), has been reported to date, as its CpCo complex, that is, CpCo(R-thiazdt).[10]

The redox behaviour of the zincate complex **2** together with its all sulfur analogue, $[NEt_4]_2[Zn(dmit)_2]$, was investigated by cyclic voltammetry in acetonitrile. In both cases, an irreversible oxidation wave is observed at $E_{pa} = 0.02$ V for **2** and $E_{pa} = 0.26$ V versus SCE for $[NEt_4]_2[Zn(dmit)_2]$. The 240 mV potential positive shift observed for $[NEt_4]_2[Zn(dmit)_2]$ when compared to **2** indicates the electron donating character of the thiazole core on the dithiolene complex. This appears to be the special feature of the thiazole core as Arca and co-workers noticed also this influence on their neutral $M(Et\text{-}thiazdt)_2$ (Ni, Pt) complexes when compared with the $M(dmit)_2$ analogues.[9]

Crystals of complex **2** were also obtained, and their X-ray crystal structure was determined (Fig. 1).[11] Moreover, complex **2** is the first dithiolene complex $M(R\text{-}thiazdt)_2$ to be crystallographically characterized. As shown in Figure 1, the zinc atom is coordinated in a distorted tetrahedral environment, with the Zn–S bond lengths being in the same range while the S–Zn–S angles show considerable variations. Indeed the ligand bite angles (95.43(10) and 95.50(12)) are considerably smaller than the remaining S–Zn–S angles (in the range 112.25(10)–121.44(10)). These values in the dianion of **2** are comparable to those observed in $[NEt_4]_2[Zn(dmit)_2]$.[12] Dihedral angle between the S1–Zn–S2 and S5–Zn–S6 mean planes amounts to 83.12(9)° compared to the 90° expected for a tetrahedral complex. The two metallacycles are slightly folded along the S···S hinge, by 10.8(3)° along S1···S2 and 9.5(3)° along S5···S6. Note also the disorder which affects one of the thiazole ring.

Dithiolene zinc complexes can be considered as efficient dithiolate protecting groups and in the presence of reactive alkyl halides, will afford the corresponding thioethers.[5] Indeed, reaction with 1,2-dibromoethane afforded **3** in 67% yield (Scheme 2). This was performed by refluxing **2** with 1,2-dibromoethane for 15 h in dichloromethane. Attempted phosphite or phosphine coupling of the thiazoline-2-thione was unsuccessful to afford the corresponding DTDAF, even by using different procedures. This behaviour has already been observed with other 1,3-thiazoline-2-thione derivatives.[4] Therefore, we used a different approach which consists in converting the thiazoline-2-thione into the thiazolium salt. The 4,5-ethylenedithio-1,3-thiazoline-2-thione **3** treated with hexafluorophosphoric acid and hydrogen peroxide gave the corresponding thiazolium salt **4** (Scheme 2).

The base-catalyzed deprotonation of the thiazolium salt **4** was realized using KOH in a two phase system (solid–liquid) under inert atmosphere.[13] This heterogeneous mixture allowed the preparation of the expected BEDT–DTDAF **5**, as shown by the cyclic voltammetry experiment carried out on the solution collected by filtration of the reaction mixture and where the electroactive species **5** formed in the medium gives rise to two reversible monoelectronic oxidation waves. The redox potentials are collected in Table 1 together with BEDT–TTF[14] and the *N*,*N*′-dimethyldibenzo-

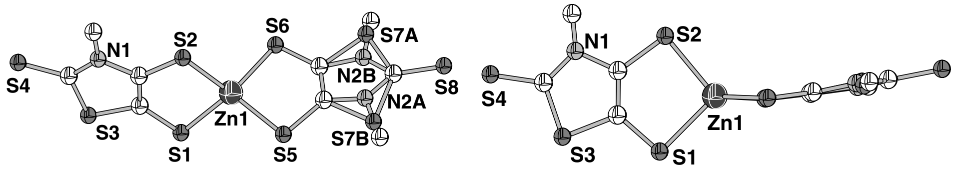
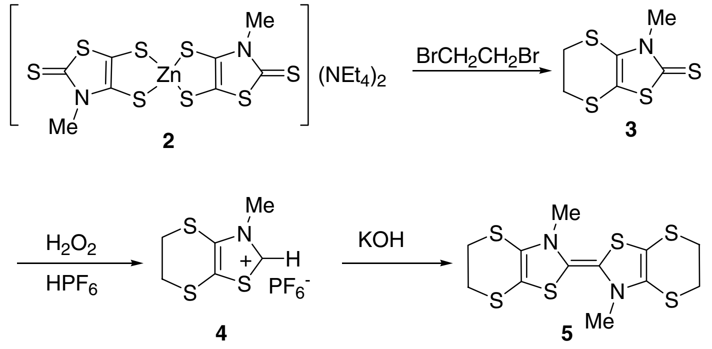


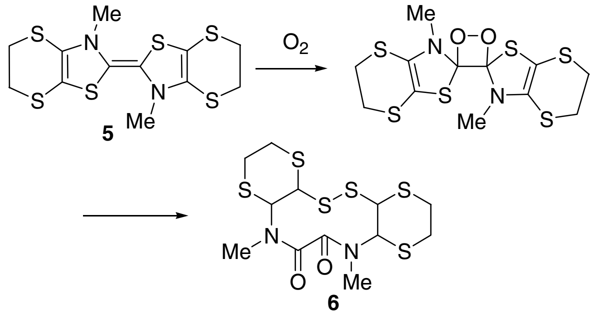
Figure 1. Molecular structure of complex **2**. Selected bond lengths (Å) and angles (°): Zn(1)–S(1) 2.361(3), Zn(1)–S(2) 2.343(3), Zn(1)–S(5) 2.315(3), Zn(1)–S(6) 2.355(3), S(5)–Zn(1)–S(6) 95.50(12), S(2)–Zn(1)–S(1) 95.43(10), S(2)–Zn(1)–S(5) 121.44(10), S(2)–Zn(1)–S(6) 112.25(10), S(1)–Zn(1)–S(5) 113.26(10), S(1)–Zn(1)–S(6) 120.95(11).



Scheme 2.

DTDAF[15] and dibenzo-TTF[16] analogues for comparison. For all these donors, three characteristic oxidation states: neutral, cation radical and dication where the two electrons are transferred in a stepwise fashion can be observed. Compared with the BEDT–TTF, the oxidation potentials for **5** are quite low as one can notice a potential difference of about 800 mV for the first oxidation step. Similar observations can be made, for example, on the dibenzo derivatives. Moreover, the potential difference $\Delta E = (E2 - E1)$ observed for **5** indicates a lower thermodynamic stability for the cation radical species issued from the DTDAF cores than from the BEDT–TTF one ($\log K = 2.2$ and 7.1 for **5** and BEDT–TTF, respectively).

Upon air exposure, the shape of the cyclic voltammogram gradually evolves with the disappearance of the two reversible oxidation waves. This instability of DTDAFs in the presence of air was already noticed as dioxygen induced oxidative rearrangements leading to various non-electroactive structures of oxygen-containing products.[17,18] Attempts were made in order to grow crystals by slow evaporation of a dichloromethane solution of the donor and to have an insight into its structure. As depicted in Figure 2, X-ray structure analysis revealed that the cyclodithiadiazecinedione **6**[8,11] resulting from the oxidative rearrangement via the formation of an intermediate dioxetane was obtained instead of the BEDT–DTDAF **5** (Scheme 3). The structures of 10-membered macrocycles were already obtained from other DTDAFs by purification of the donor in the presence of air.[18]



Scheme 3.

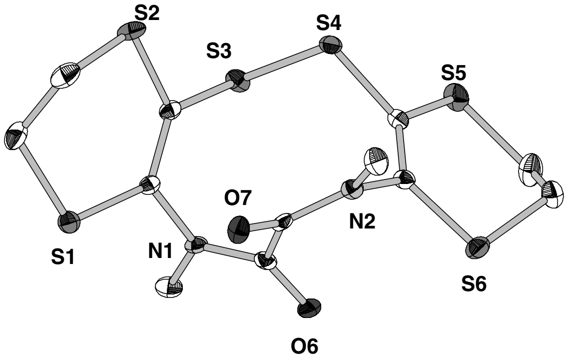


Figure 2. Molecular structure view of **6** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity.

In conclusion a simple and efficient approach to *N*-methyl-1,3-thiazoline-2-thione-4,5-dithiolate, easily isolated as its zinc dithiolene complex, has been described. This complex can be a valuable tool for the access to new functionalized DTDAFs such as BEDT–DTDAF. The air sensitivity of this donor was demonstrated by the obtention of the crystal structure of a cyclodiazecinedione. Future investigations for the use of this donor as a precursor of molecular materials will be realized under anaerobic conditions.

Table 1. Oxidation potentials, *E* in V versus SCE, Pt working electrode with 0.1 M Bu_4NPF_6

	E_1	E_2	$\Delta E(E_2 - E_1)$ (mV)	$\log K$[b]
BEDT–DTDAF **5**	−0.33	−0.20	130	2.2
BEDT–TTF	0.455	0.875	420	7.1
N,*N*′-dimethyldibenzo-DTDAF[a,15]	−0.17	−0.02	150	2.5
Dibenzo-TTF[a,16]	0.72	1.06	340	5.7

[a] *E* in V versus Ag/AgCl.

[b] $\log K = \Delta E/0.059$.

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References and notes

1. See the special issue on 'Molecular Conductors' *Chem. Rev.* **2004**, *104*, 4887–5781, and references cited therein.
2. Rovira, C. *Chem. Rev.* **2004**, *104*, 5289–5317.
3. Whangbo, M.-H.; Williams, J. M.; Schultz, A. J.; Emge, T. J.; Beno, M. A. *J. Am. Chem. Soc.* **1987**, *109*, 90.
4. Lorcy, D.; Bellec, N. *Chem. Rev.* **2004**, *104*, 5185.
5. Svenstrup, N.; Becher, J. *Synthesis* **1995**, 215.
6. (a) Bellec, B.; Lorcy, D.; Robert, A. *Synthesis* **1998**, 1442; (b) Eid, S.; Guerro, M.; Roisnel, T.; Lorcy, D. *Org. Lett.* **2006**, *8*, 2377.
7. Bellec, N.; Lorcy, D.; Boubekeur, K.; Carlier, R.; Tallec, A.; Los, Sz.; Pukacki, W.; Trybula, M.; Piekara-Sady, L.; Robert, A. *Chem. Mater.* **1999**, *11*, 3147.
8. Selected data for **2**. *Bis(tetraethylammonium)bis(3-methyl-1,3-thiazoline-2-thione-4,5-dithiolato)zincate*: light brown crystals; mp 232 °C; ^{1}H NMR (300 MHz; CD_3CN) δ 1.19 (t, 24H, CH_3), 3.14 (q, 16H, CH_2), 3.70 (s, 6H, CH_3); ^{13}C NMR (75 MHz; CD_3CN) δ 6.8, 37.9, 52.2, 116.3, 141.1, 179.7; Anal. Calcd for $C_{24}H_{46}N_4S_8Zn$: C, 40.45; H, 6.51; N, 7.86; S, 36.00. Found: C, 40.42; H, 6.53; N, 7.91; S, 36.32. Selected data for **3**. *N-methyl-4,5-ethylenedithio-1,3-thiazol-2-thione*: mp 152 °C; ^{1}H NMR (300 MHz; CD_3Cl) δ 3.41 (m, 4H, CH_2–CH_2), 3.62 (s, 3H, CH_3); ^{13}C NMR (75 MHz; CD_3Cl) δ 28.8, 29.6, 34.5, 108.2, 125.9, 184.7; HRMS calcd for $C_6H_7NS_4$: 220.9461. Found: 220.9455. Anal. Calcd for $C_6H_7NS_4$: C, 32.55; H, 3.19; N, 6.33. Found: $C_6H_7NS_4$: C, 32.25; H, 3.14; N, 6.24. Selected data for **4**. *N-Methyl-4,5-ethylenedithio-1,3-thiazolium*: mp 171 °C; ^{1}H NMR (300 MHz; CD_3CN) δ 3.51 (m, 4H, CH_2–CH_2), 4.01 (s, 3H, CH_3), 9.44 (s, 1H); ^{13}C NMR (75 MHz; CD_3CN) δ 27.8, 28.1, 40.1, 126.8, 135.5, 153.9; HRMS calcd for $C_6H_8NS_3$: 189.9818. Found: 189.9821. Anal. Calcd for $C_6H_8F_6NPS_3$: C, 21.49; H, 2.4; N, 4.18. Found: C, 21.21; H, 2.65; N, 4.22. Selected data for **6**. *Cyclodiazecinedione*: orange crystals; mp >260 °C; ^{1}H NMR (300 MHz; CD_3Cl) δ 3.32 (m, 8H, CH_2), 3.54 (s, 6H, CH_3); ^{13}C NMR (75 MHz; CD_3Cl) δ 13.05, 21.3, 33.1, 107.4, 125.1, 162.7; HRMS calcd for $C_{12}H_{14}N_2O_2S_6$: 409.9380. Found: 409.9389.
9. Aragoni, M. C.; Arca, M.; Devillanova, F. A.; Isaia, F.; Lippolis, V.; Mancini, A.; Pala, L.; Slawin, A. M. Z.; Woolins, J. D. *Inorg. Chem.* **2005**, *44*, 9610.
10. Werner, H.; Xiolan, L.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1997**, *130*, 871.
11. The X-ray crystallographic data for **2** and **6** have been deposited, as supplementary publication number CCDC 616005 and CCDC 616006, respectively, at the Cambridge Crystallographic Data. Copies of the data can be obtained free of charge from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; e-mail: deposit@ccdc.cam.ac.uk.
12. Comerlato, N. M.; Harrison, W. T. A.; Howie, R. A.; Low, J. N.; Silvino, A. C.; Wardell, J. L.; Wardell, S. M. S. V. *Acta Crystallogr.* **2002**, *C58*, m105.
13. Morel, G.; Gachot, G.; Lorcy, D. *Synlett* **2005**, 1117.
14. Kumar, E. V. K. S.; Singh, J. D.; Singh, H. B.; Das, K.; Verghese, B. *Tetrahedron* **1997**, *53*, 11627.
15. Hünig, S.; Schlaf, H.; Kiesslich, G.; Scheutzow, D. *Tetrahedron Lett.* **1969**, *27*, 2271.
16. Hünig, S.; Kiesslich, G.; Quast, H.; Scheutzow, D. *Liebigs Ann. Chem.* **1973**, 310.
17. (a) Vorsanger, J. J. *Bull. Soc. Chim. Fr.* **1964**, 119; (b) Wanzlick, H. W.; Kleiner, H. J.; Lasch, I.; Füldner, H. U.; Steinmaus, H. *Liebigs Ann. Chem.* **1967**, *708*, 155; (c) Takamizawa, A.; Hirai, K.; Hamashima, Y.; Sato, H. *Chem. Pharm. Bull.* **1969**, *17*, 1462; (d) Baldwin, J. E.; Walker, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 596.
18. (a) Koizumi, T.; Bashir, N.; Kennedy, A. R.; Murphy, J. A. *J. Chem. Soc., Perkin Trans. 1* **1999**, 3637; (b) Bssaibis, M.; Robert, A.; Lemaguerès, P.; Ouahab, L.; Carlier, R.; Tallec, A. *J. Chem. Soc., Chem. Commun.* **1993**, 601.