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Tetrahedron Letters

Tetrahedron Letters 47 (2006) 3123–3125

Evidence of the central tetrathiafulvalene bond opening by copper(II) salts. In situ generation of 2,3-bis(2′-cyanoethylchalcogeno)-7,8-benzo-1,4,6,9-tetrathia-10-ceto spiro[4,5]decane

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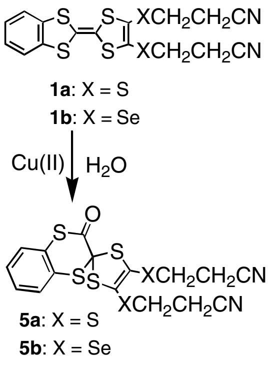
Received 25 January 2006; revised 20 February 2006; accepted 24 February 2006
Available online 15 March 2006

Abstract—The two-electrons oxidation of 4,5-benzo-6,7-bis(2′-cyanoethylthio) TTF (CETBz-TTF) and 4,5-benzo-6,7-bis(2′-cyanoethylseleno) TTF (CESBz-TTF) with $Cu^{2+}X_2$ ($X = Cl^-$, BF_4^-) leads to the formation of 2,3-bis(2′-cyanoethylchalcogeno)-7,8-benzo-1,4,6,9-tetrathia-10-ceto spiro[4,5]decane after opening of the –C–S– bond of the central TTF core.

1. Introduction

The well-known TTFs (tetrathiafulvalene) charge-transfer salts are still subjects of intensive investigations. Current activities in this field comprise development of multifunctional materials.[1] Interplay between magnetic properties of localized transition-metal d-spins and mobile electrons of mixed-valence TTFs have been reported for several BEDT-$TTF_3[MnCr(C_2O_4)_3]$ (bis-(ethylene dithio-TTF)),[2] $(BETS)_2FeCl_4$ (BETS = bis-(ethylene dithio-tetraselenafulvalene)),[3] (C1-TET-$TTF)_2FeX_4$ (X = Cl, Br; C1-TET-TTF = 4,5-bis(methylthio)-4′,5′-ethylenedithio-TTF).[4] These compounds consist of discrete organic radical cations with inorganic anions containing paramagnetic transition metals. However, through-space interactions between d and π electrons in these type of salts is very weak. In order to increase these interactions, it was proposed to prepare paramagnetic coordination complexes where the paramagnetic centre and the TTF are covalently linked.[1c] Hence numerous functionalized TTFs have been prepared as well as their metal complexes.[5]

In the course of our work on this kind of materials we have tried to prepare Cu(II) complexes of 4,5-benzo-6,7-bis(2′-cyanoethylthio) TTF (CETBz-TTF) **1a** and 4,5-benzo-6,7-bis(2′-cyanoethylseleno) TTF (CESBz-TTF) **1b**,[6] and we found (Scheme 1) that the reaction of $Cu(II)CL_2$ with these donors in a mixture of acetonitrile and water leads to two new radical cation salts (RCS)[7] namely, $(\mathbf{1})_2{\cdot}CuCl_4$ and $(\mathbf{1})_2{\cdot}Cu_2Cl_6(H_2O)_2$, and the title compounds 2,3-bis(2′-cyanoethylthio)-7,8-benzo-1,4,6,9-tetrathia-10-ceto spiro[4,5]decane (**5a**) and 2,3-bis(2′-cyanoethylseleno)-7,8-benzo-1,4,6,9-tetrathia-10-ceto spiro[4,5]decane (**5b**). The obtention of these



Scheme 1.

Keywords: Benzo-tetrathiafulvalene; Copper(II); Rearrangement; Electron oxidation; Opening central TTF bond.

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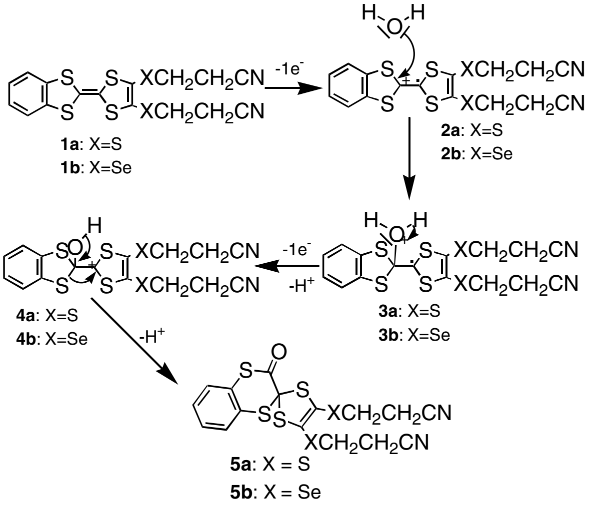
doi:10.1016/j.tetlet.2006.02.145

RCS was expected since it is well known that copper(II) salts can oxidize TTFs leading to charge transfer or radical cation salts.[8–10] However, the rearranged TTFs **5a** or **5b** by the oxidation process was unexpected.

The Cu(II)-mediated oxidative cyclization may proceed through the mechanistic pathway shown in Scheme 2. One-electron oxidation of the TTF moiety affords electrophilic radical cations **2a** or **2b**, which react with one molecule of water leading to compounds **3a** or **3b** with a hydroxylic function on the central TTF bond. The second oxidation of radicals **3a** or **3b** gives cations **4a** or **4b**, which undergo a rearrangement of the donor molecule by the loss of a proton. Finally, opening of the C–S bond increases the heterocycle size, leading to the new compounds **5a** or **5b**, which were characterized by IR, NMR and mass spectroscopy as well as X-ray structure analysis.

Compounds **5a** and **5b** are isostructural, they both crystallize in the orthorhombic space group *Pcab*. The ORTEP drawing of **5a** as well as selected bond lengths and bond angles are given in Figure 1. The five- and six-membered heterocycles are connected by the sp^3 C8 atom with a mean C–S bond length equal to 1.823(4) Å. The bond angles around C8 atoms vary from 106.3(2)° to 114.3(2)°, the C7–O1 bond length (1.206(4) Å) lies within the expected value for a C═O double bond. The remaining C–S, C–C and C═O bond lengths and bond angles are in the expected range. The S4–C10–S6–S5–C5–S2 (plane **I**) and S1–C6–C4–S3 (plane **II**) parts are planar. The two –(CH$_2$)$_2$CN groups are on the same side of plane **I** and the benzo-ring is co-planar with plane **II**.

The use of copper salts is very usual in TTF chemistry. In addition to their oxidative properties, they contribute to the formation of radical cation salts by providing the anionic part after in situ rearrangement. However, little is known on the oxidative mechanism.



Scheme 2. Proposed mechanism pathway.

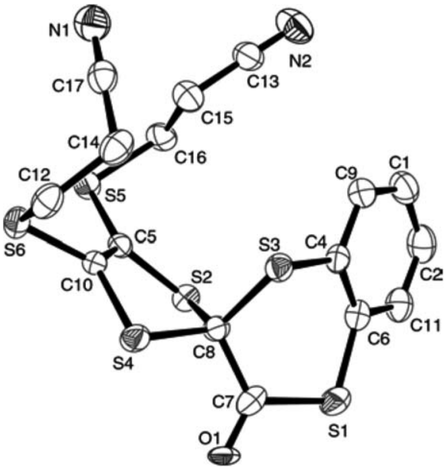


Figure 1. ORTEP view of **5a** with 30% probability (H-atoms omitted for clarity). Selected bond lengths (Å): C8–S2 = 1.817(4); C8–S3 = 1.827(4); C8–S4 = 1.827(3); C8–C7 = 1.523(5), C7–O1 = 1.206(4); S1–C6 = 1.756(4); S3–C4 = 1.760(4); C4–C6 = 1.393(5); S2–C5 = 1.766(3); S4–C10 = 1.758(3); C5–C10 = 1.355(5); N1–C17 = 1.135(5); N2–C13 = 1.128(5) and bond angles (°): S2–C8–S4 = 106.3(2), C7–C8–S2 = 110.2(2), C7–C8–S3 = 109.3(2), S2–C8–S3 = 114.3(2), C7–C8–S4 = 109.5(2), S3–C8–S4 = 109.5(2), S3–C8–S4 = 107.1(2), C5–S5–C16 = 101.2(2), C10–S6–C12 = 101.8(2).

To the best of our knowledge, opening of the TTF S–C bond has been shown from mesoionic thiazoles leading to the formation of 10-membered macrocycles by oxidation with oxygen.[11]

In our case, we employed degassed solvents and worked under argon atmosphere. Therefore it is not the oxygen in air, which reacts with our donors. An other type of reactivity close to our synthesis is the conversion of a tetrathiafulvalene (TTF) derivative into 3,3′-bithiazolopyridinium, a stable heterocyclic 10+10 π electron system by using perchlorate copper(II) salt.[12] In this case also, it has been found that it is the presence of copper(II), which oxidizes the TTF derivatives. However, the opening concerned the outer part of the central TTF core (positions 1–2 in Scheme 1). This is different from the present situation where the opening occurs in the central TTF part (positions 6–10 in Scheme 2).

In addition to the work by Decurtins group,[12] the isolation and characterization of the title compounds **5a** and **5b** confirm clearly that the oxidation of TTFs by Cu(II) salts leads to the opening of the S–C bond of the central TTF core. However, the parameters controlling the selectivity of the inner or outer S–C bonds opening (positions 6–10 or 1–2 in Scheme 1) are still unclear and more examples are needed to explain this point.

NMR spectra were recorded on a Bruker AC 200 instrument. EI mass spectra were recorded on a JOEL JMS-DX 300 spectrometer. IR spectra were recorded with a Bruker EQUINIOX 55 spectrometer. Melting points were measured with a Buchi apparatus.

An acetonitrile solution (20 ml) containing CETBz-TTF (53 mg, 0.13 mmol) or CESBz-TTF (67 mg, 0.13 mmol) was mixed with a water solution (1.5 ml) of $CuCl_2{\cdot}2H_2O$ (44 mg, 0.26 mmol) or $Cu(BF_4)_2{\cdot}6H_2O$ (89.73 mg, 0.26 mmol). After stirring for 1 day, the mixture was filtered. The filtrate was evaporated slowly. Black platelets of radical cation salts were isolated before complete evaporation of the solvent. The residue was chromatographed on silica-gel with dichloromethane as eluent to lead white crystals of salts **5a** or **5b** in 57% (30 mg) and 39% (27 mg) yields, respectively.

2. 2,3-Bis(2′-cyanoethylthio)-7,8-benzo-1,4,6,9-tetrathia-10-ceto spiro[4,5]decane 5a

White crystals, mp = 138 °C. ^{1}H NMR ($CDCl_3$), $\delta =$ 2.95 (t, $J = 7.0$ Hz, 4H, CH_2CN), 3.11 (t, $J = 7.0$ Hz, 4H, CH_2S), 7.40 (m, 4H, Har); ^{13}C NMR ($CDCl_3$), $\delta = 18.58$ (CH_2CN); 31.49 (CH_2S); 117.50 (CN); 185.67 (CO), 126.23, 127.90, 128.81, 129.28, 129.35, 131.50, 132.83 (C=). MS (electrospray +, MeOH/CH_2Cl_2: 95/5) $[M+Na]^+$: calcd for $C_{16}H_{12}N_2ONaS_6$ 462.9172, measured 462.9167; IR (KBr)/cm^{-1}: $\nu_{C=O}$: 1716(vs); ν_{CN}: 2268.

3. 2,3-Bis(2′-cyanoethylseleno)-7,8-benzo-1,4,6,9-tetrathia-10-ceto spiro[4,5]decane 5b

White crystals, mp = 128 °C. ^{1}H NMR ($CDCl_3$), $\delta =$ 2.98 (t, $J = 7.0$ Hz, 4H, CH_2CN), 3.13 (t, $J = 7.0$ Hz, 4H, CH_2Se), 7.30 (m, 4H, Har); ^{13}C NMR ($CDCl_3$), $\delta = 19.26$ (CH_2CN); 23.44 (CH_2Se); 118.00 (CN); 185.75 (CO), 122.00, 126.20 (C=). MS (electrospray +, MeOH/CH_2Cl_2: 95/5) $[M+Na]^+$: calcd for $C_{16}H_{12}N_2OnaS_4Se_2$ 556.9258, measured 556.9245; IR (KBr)/cm^{-1}: $\nu_{C=O}$: 1721(vs); ν_{CN}: 2272.

4. Crystal data for 5a

$C_{16}H_{12}N_2OS_6$, $M = 440.64$, orthorhombic, space group *Pcab*, $a = 8.0255(1)$, $b = 17.3962(2)$, $c = 28.0085(5)$ Å, $V = 3910.4(1)$ Å^3, $Z = 8$, $T = 293(2)$ K, $\mu(\mathrm{MoK}\alpha) = 0.707$ mm^{-1}, $D_{calc} = 1.497$ g cm^{-3}, 6452 reflections measured of which 3454 unique ($R_{int} = 0.0312$), $R(F^2) = 0.0408$ [2313 data with $I > 2\sigma(I)$], $wR(F^2) = 0.136$.

5. Crystal data for 5b

$C_{16}H_{12}N_2OS_4Se_2$, $M = 534.44$, orthorhombic, space group *Pcab*, $a = 8.1610(2)$, $b = 17.3811(4)$, $c = 28.1819(7)$ Å, $V = 3997.5(2)$ Å^3, $Z = 8$, $T = 293(2)$ K, $\mu(\mathrm{MoK}\alpha) = 4.125$ mm^{-1}, $D_{calc} = 1.776$ g cm^{-3}, 6589 reflections measured of which 3548 unique ($R_{int} = 0.0377$), $R(F^2) = 0.0440$ [2389 data with $I > 2\sigma(I)$], $wR(F^2) = 0.108$. Data collected on a Nonius four circle diffractometer from CDFIX (Rennes) equipped with a CCD camera and a graphite monochromated MoK_α radiation source ($\lambda = 0.71073$ Å). Effective absorption correction was performed (SCALEPACK).[13] Structures were solved by direct methods with SHELXS-97 and refined by full-matrix least-squares method on F^2 with SHELXL-97 programs.[14]

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