Tetrathiafulvaleno-quinonemethides and -thioquinonemethides

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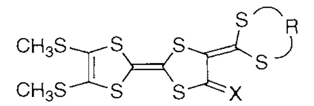
Novel donor/acceptor-type tetrathiafulvalenes, tetrathiafulvaleno-quinonemethide and -thioquinonemethide were synthesized, which are expected as new π donor molecules bearing d local spin, because they can capture several magnetic metal ions through binding with the carbonyl oxygen or thiocarbonyl sulfur atom.

The synthesis of organic complexes involving both conducting π electron and local d spin is of current interest, since novel electrical conducting and magnetic properties, especially superconductivity and ferromagnetism with much more increased critical temperatures might be produced, if the conducting π electron and local d spin can significantly interact with each other.[1] There are so far known several π/d systems of copper-[2] and cobalt-phthalocyanines,[3] copper dicyanoquinodiimines,[4] and bis(ethylenedithio)-tetrathiafulvalene and -tetraselenafulvalene radical cation salts with copper or iron ion.[5-8] The degree of π/d interaction is different by each complex, and novel electrical conducting and magnetic properties have emerged from some complexes exhibiting significant π/d interaction. Now, we report the synthesis and some physicochemical properties of two donor/acceptor-type tetrathiafulvalenes, bis(methylthio)tetrathiafulvaleno-quinonemethide (1) and -thioquinonemethide (2), which are expected to capture magnetic metal ions through binding with the carbonyl oxygen or thiocarbonyl sulfur atom. It is possible that the contribution of a polar structure to the ground states of 1 and 2 furthermore increases by binding of a metal ion at the carbonyl oxygen or thiocarbonyl sulfur atom. The positive charge residing in the 1,3-dithiolane or 1,3-dithiole ring might serve as an oxidizing agent of the tetrathiafulvalene ring, eventually bringing much expectation of a new π/d system for some complexes of 1 or 2 with magnetic metal ions.

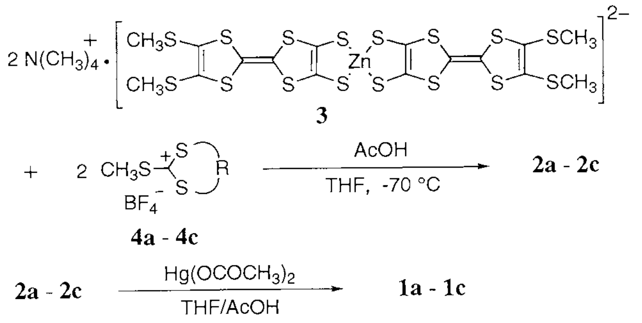


(1) X = O
(2) X = S

(a) R = $-CH_2CH_2-$; (b) R = $-CH=CH-$; (c) R = 4-methylbenzo

As is shown in Scheme 1, bis(tetramethylammonium) bis-(2,3-dimethylthiotetrathiafulvalenyl-6,7-dithiolato) zinc complex (**3**)[9] was reacted with 2 equiv. of 2-methylthio-1,3-dithiolanium (**4a**), -1,3-dithiolium (**4b**) or -1,3-(4-methylbenzo)dithiolium tetrafluoroborate (**4c**)[10,11] in THF containing 1% (v/v) acetic acid at -70 °C under argon. After separation of the reaction mixture by column chromatography on silica gel and recrystallization from CS_2/MeOH, **2a** - **2c** were isolated as black crystals in 35, 34 and 37% yields, respectively. When **2a** - **2c** were reacted with 1 equiv. of mercury(II) acetate in THF/AcOH (1:1 v/v) at 20 °C, **1a** - **1c** were obtained as red crystals in >80% yield by recrystallization from CS_2/MeOH. It is most conceivable as a plausible formation scheme of **2** that the thiolate anion of one tetrathiafulvalenyldithiolato group in **3** attacks the carbon atom at the 2-position of **4**, and subsequently the vinylthiolate carbon anion again attacks the 2-carbon atom of **4** accompanied with elimination of the methylthio group, followed by expulsion of sulfur atom from the episulfide intermediate to afford the final product.

Scheme 1.



The molecular structures[12] of **1b** and **2b** are shown in Figure 1. For both the molecules the tetrathiafulvaleno-quinone (or -thioquinone)methide skeleton is almost planar. The bond distances of carbonyl- and thiocarbonyl-1,3-dithiole-2-ylidene groups are as follows: C=O (1.22), C-C (1.43) and C=C (1.35 Å) for **1b**, and C=S (1.66), C-C (1.39) and C=C (1.38 Å) for **2b**. The observed values are very close to those of normal α,β-unsaturated ketones[13] and thioketones[14], suggesting that the degree of polarization of carbonyl- and thiocarbonyl-1,3-dithiole-2-ylidene groups in **1b** and **2b** is as usual and almost not influenced by attaching the tetrathiafulvaleno group.

The electron-donating properties of **1** and **2** were investigated

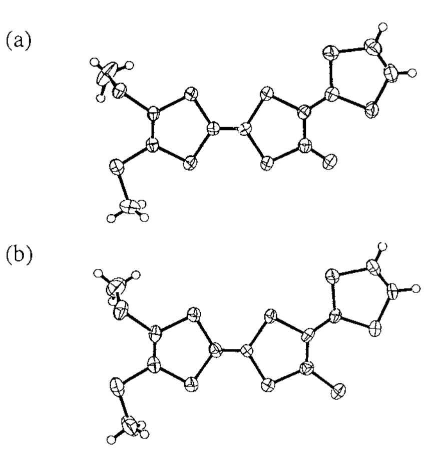


Figure 1. The molecular structures of (a) **1b** and (b) **2b**.

by using cyclic voltammetry, and compared with that of tetrakis(methylthio)tetrathiafulvalene (**5**). The measurement was carried out at 0 °C in DMF containing 0.1 M NEt_4ClO_4 as a supporting electrolyte by using Pt wires as both working and counter electrodes. The cyclic voltammograms of **1** and **2** were composed of two pairs of reversible waves, which correspond to one- and two-electron transfers, respectively. The first (E^1) and second potentials (E^2) are summarized in Table 1. The E^1 values are +0.62 - +0.66 V vs. Ag/AgCl for **1a** - **1c**, and +0.59 - +0.64 V for **2a** - **2c**. When the E^1 values are compared between **1** and **2** bearing the same electron-donating group of 1,3-dithiolane-, 1,3-dithiole- or 1,3-(4-methylbenzo)dithiole-2-ylidene, slightly lower values are obtained for **2** than **1**. However, both the E^1 values are higher by ca. 0.2 V than that of **5** (+0.49 V), indicating that **1** and **2** can still serve as π donor molecules, although their electron-donating ability is inferior to that of **5**.

Table 1. Redox potentials of **1a** - **1c** and **2a** - **2c** in DMF at 0 °C

Donor	$E^{1\,a}$	$E^{2\,a}$
1a	+ 0.62	+ 0.78
1b	+ 0.62	+ 0.85
1c	+ 0.66	+ 0.85
2a	+ 0.59	+ 0.76
2b	+ 0.61	+ 0.77
2c	+ 0.64	+ 0.80
5	+ 0.49	+ 0.69

^{a}V vs. Ag/AgCl.

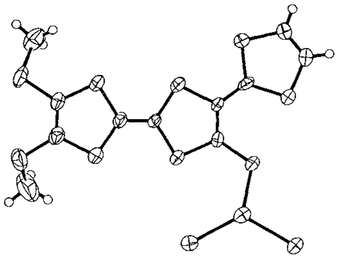


Figure 2. The molecular structure of **6**.

For a preliminary experiment, **2b** was treated with 1 equiv. of $CuBr_2$ in CH_3CN/CS_2 to afford the **2b**/$CuBr_2$ (1:1) complex (**6**) quantitatively. As is obvious from the molecular structure of **6**[12] (see Figure 2), the Cu(II) ion is bound to the thiocarbonyl sulfur atom. The synthesis of the $CuBr_2$ complexes with the other **1** and **2** molecules than **2b**, and their electrical conducting and magnetic properties are now under investigation.

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12 Crystal data for **1b**: $C_{11}H_8S_9$, M = 428.72, monoclinic, space group $P2_1/n$, a = 5.138(4), b = 28.170(4), c = 11.436(2) Å, β = 95.80(3)°, Z = 4, V = 1646(1) Å^3, Dc = 1.729 g/cm^3. R = 0.050 and Rw = 0.102 for 1601 observed reflections with $I > 2\sigma(I)$. Crystal data for **2b**: $C_{11}H_8OS_8$, M = 412.66, triclinic, space group $P\bar{1}$, a = 8.427(2), b = 13.408(3), c = 7.482(2) Å, α = 92.26(2), β = 104.33(2), γ = 81.89(1)°, Z = 2, V = 810.9(3) Å^3, Dc = 1.690 g/cm^3. R = 0.054 and Rw = 0.064 for 2120 observed reflections with $I > 2\sigma(I)$. Crystal data for **6**$\cdot CS_2 \cdot H_2O$: $C_{11}H_8S_9CuBr_2 \cdot CS_2 \cdot H_2O$, M = 746.30, triclinic, space group $P\bar{1}$, a = 11.628(4), b = 12.719(4), c = 8.479(2) Å, α = 104.79(2), β = 106.80(2), γ = 101.32(3)°, Z = 2, V = 1110.2(7) Å^3, Dc = 2.094 g/cm^3. R = 0.049 and Rw = 0.084 for 2256 observed reflections with $I > 2\sigma(I)$. The measurements were made by Rigaku AFC7R diffractometer with graphite monochromated Cu-$K\alpha$ radiation (λ = 1.54178 Å) for **1b** and **2b**, and by Rigaku AFC5R diffractometer with graphite monochromated Mo-$K\alpha$ radiation (λ = 0.71069 Å) for **6**$\cdot CS_2 \cdot H_2O$.

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