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Characterization of a Byproduct in the Alkylation of DMIT: Alkylation on the Least Nucleophilic Sulfur Atom

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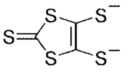
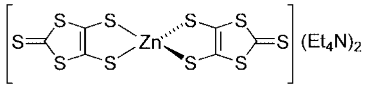
It is generally accepted that the alkylation of $(Et_4N)_2[Zn(DMIT)_2]$ (**1**) is a very clean reaction that produces 4,5-bis(alkylthio)-1,3-dithiole-2-thiones **4** in very high yields. Although this procedure has been widely used, we have found that, in addition to the 4,5-bis(alkylthio)-1,3-dithiole-2-thione products **4**, highly unexpected byproducts are formed during the alkylation reaction in which the thione functionalities of DMIT in $(Et_4N)_2[Zn(DMIT)_2]$ (**1**) are alkylated instead of the more reactive thiolate groups. These byproducts were identified as a novel type of compounds, namely bis(2-alkylthio-1,3-dithiol-1-ium-4,5-dithiolato)zinc compounds **3**, being composed of two identical 2-alkylthio-1,3-dithiol-1-ium-4,5-dithiolate moieties coordinated to a single zinc(II) atom and were characterized by elemental analyses and different spectroscopic techniques as well as single-crystal X-ray structure analyses. A comparison of the physical properties of compounds **3** and $(Et_4N)_2[Zn(DMIT)_2]$ (**1**) has been carried out. The outcome of these investigations revealed significant differences in the physical properties of these two systems.

Introduction

Among sulfur-containing heterocycles, derivatives of 2-thioxo-1,3-dithiole-4,5-dithiolate[1] (DMIT), have received a central position in organic and materials chemistry on account of the discovery of superconductivity in some of the metal complexes[2,3] of DMIT and its chalcogene analogs.[4] In addition, derivatives of DMIT are important building blocks for the synthesis[5] of tetrathiafulvalene[6–9] (TTF) systems, such as bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) which has been employed for the preparation of an extensive range of conducting[10] and superconducting materials.[11,12] DMIT is commonly isolated as its zinc chelate[13] in the form of bis(tetraethylammonium) bis(2-thioxo-1,3-dithiole-4,5-dithiolato)zincate $(Et_4N)_2[Zn(DMIT)_2]$ (**1**) and subsequent alkylation of the chelated thiolate groups can be accomplished with a variety of alkylating agents producing[14] in most cases 4,5-bis(alkylthio)-1,3-dithiole-2-thiones.


DMIT


$(Et_4N)_2[Zn(DMIT)_2]$
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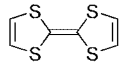
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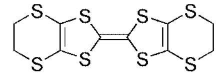
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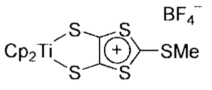
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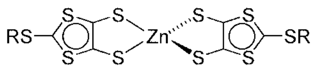
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Although alkylation of the thione functionality of 1,3-dithiole-2-thione derivatives are favored by a gain in energy caused by aromatization of the 1,3-dithiole ring to a 1,3-dithiolium system simple alkylating agents, such as alkyl halides, are not sufficiently strong alkylating agents to accomplish this type of reaction for 4,5-bis(alkylthio)-1,3-dithiole-2-thiones. Instead, stronger alkylating agents, such as methyl fluorosulfate, methyl trifluorosulfonate, triethyloxonium tetrafluoroborate, triethyl orthoformate, boron trifluoride–diethyl ether, and dimethyl sulfate must be employed to produce[15] 2,4,5-tris(alkylthio)-1,3-dithiolium salts. Despite several reports on 2,4,5-tris(alkylthio)-1,3-dithiolium salts only one example[16] of a 2-alkylthio-1,3-dithiolium-4,5-dithiolate system – in the form of bis(cyclopentandienyl)(2-methylthio-1,3-dithiolium-4,5-dithiolato)-titanium(IV) (**2**) – has, to the best of our knowledge, been reported so far. In this paper, we present the synthesis and characterization of four systems **3** each containing two 2-alkylthio-1,3-dithiolium-4,5-dithiolate moieties coordinated to a single zinc(II) atom.

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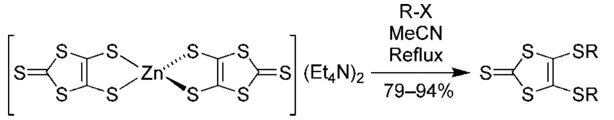
Results and Discussion

In most cases, the reaction between $(Et_4N)_2[Zn(DMIT)_2]$ (**1**) and an appropriate alkyl halide proceeds smoothly producing (Scheme 1) the corresponding 4,5-bis(alkylthio)-1,3-dithiole-2-thiones **4** in yields ranging from 79% to 94%.[14] In the present investigations, we have observed that, in addition to the desired 4,5-bis(alkylthio)-1,3-dithiole-2-thione products **4**, highly unexpected byproducts are formed during the reaction as a result of alkylation of the thione functionalities instead of the more reactive thiolate groups.

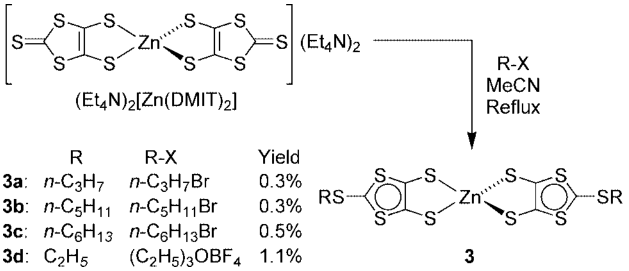


$(Et_4N)_2[Zn(DMIT)_2]$

4

Scheme 1. Synthesis of 4,5-bis(alkylthio)-1,3-dithiole-2-thione products **4**.

In a typically alkylation experiment (Scheme 2), the zincate $(Et_4N)_2[Zn(DMIT)_2]$ (**1**) and the alkyl halide were heated under reflux in MeCN followed by an aqueous workup. Subsequent purification by means of column chromatographic purification afforded a broad yellow fraction together with a weaker blue fraction. The first yellow fraction contained 4,5-bis(alkylthio)-1,3-dithiole-2-thione **4**, whereas it was identified (vide infra) that the second blue band contained the unexpected bis(2-alkylthio-1,3-dithiol-1-ium-4,5-dithiolato)zinc compound **3** as byproduct.



	R	R-X	Yield
3a:	n-C_3H_7	n-C_3H_7Br	0.3%
3b:	n-C_5H_{11}	n-$C_5H_{11}Br$	0.3%
3c:	n-C_6H_{13}	n-$C_6H_{13}Br$	0.5%
3d:	C_2H_5	$(C_2H_5)_3OBF_4$	1.1%

3

Scheme 2. Synthesis of bis(2-alkylthio-1,3-dithiol-1-ium-4,5-dithiolato)zinc compounds **3**.

As illustrated in Scheme 2, the isolated yields for **3a**–**c** are less than 0.5% when simple alkyl bromides are used as the alkylating agent. However, the yield can be improved by using the stronger alkylating agent triethyloxonium tetrafluoroborate. In this case, **3d** was isolated in a yield just above 1%. The fact that the yields of **3a**–**d** are very low can most likely be accounted for by the presence of the more nucleophilic thiolate groups in $(Et_4N)_2[Zn(DMIT)_2]$ (**1**) which prevents the formation of any larger amounts of **3**. Although **3a**–**d** were isolated in very low yields, the alkylation reactions can be carried out on a large scale allowing substantial amounts (50–150 mg) of **3a**–**d** to be isolated.

The unexpected byproducts **3a**–**d** were all isolated as purple solids. ^1H and ^{13}C NMR spectroscopy, high-resolution mass spectrometry, and elemental analyses all support the proposed structures of **3a**–**d**. Furthermore, the structures of **3a** and **3b** were unequivocally determined by single-crystal X-ray structure analyses.

X-ray Crystallographic Studies

Crystals of **3a** and **3b** were grown by letting cyclohexane diffuse into $CHCl_3$ solutions of **3a** and **3b**, respectively. Both compounds show very strong pleochroism with colors changing between bright blue and dark red under polarized light. Crystallographic data were collected with a Nonius KappaCCD diffractometer with Mo-K_α radiation (λ = 0.71073 Å) and the structures were solved by direct methods using SIR97[17] followed by refinement with SHELXL97.[18] Table 1 summarizes the crystallographic data obtained for compound **3a** and **3b**.

The two chelating planes form angles of 85.1(4)° in **3a** and 89.58(13)° in **3b** as compared to 83–85° between the chelating planes in $(Et_4N)_2[Zn(DMIT)_2]$ (**1**). The molecular structure of **3b** with a partial labeling scheme is shown in Figure 1a. In both structures Zn is tetrahedrally coordinated with distortions on account of the limited bite angle of the bis(thiolato) ligand. The coordination geometry closely resembles that of $(Et_4N)_2[Zn(DMIT)_2]$ (**1**). However, in the case of **3b**, there is no crystallographically imposed symmetry contrasting with the twofold axial symmetry observed in about half of the known structures related to $(Et_4N)_2[Zn(DMIT)_2]$ (**1**).[19] This lack of restraint makes DOQXOW[20] the best candidate for comparison as it too is unrestrained and its data collected at 150 K (see Table 2 for a comparison of average bond lengths).

There is no apparent change in Zn–S distances despite the reduced charge of the ligand. The only significant geometric difference between the new ligand and $(Et_4N)_2[Zn(DMIT)_2]$ (**1**) is the obvious lengthening of the C(3)–S(5) bond to a value somewhere between a double (DMIT) and single bond [S(5)–C(7)]. An accompanying shortening of S(3)–C(3) cannot be considered significant.

The packing of **3a** and **3b** is almost identical and the packing diagram of **3b** is depicted in Figure 1b. Both have an ordered alkyl chain in perfect staggered conformation in the plane of its attached dithiole ring. These ordered alkyl chains pack together with symmetry-equivalent copies to form layers parallel to the *ab* plane. The other alkyl chain is twisted and has bonds which are orthogonal to its attached dithiole ring. This twist results in a disorder that cannot readily be modeled wherefore large ADPs have been accepted instead. The disordered alkyl chains pack in a mixed layer in which one of the dithiole rings is sandwiched between the simple alkyl layers. The mixed layer is dominated by C–H···S interactions (minima are 2.9 Å and 2.7 Å in **3a** and **3b**, respectively) and S···S interactions (3.5 Å and 3.7 Å); **3b** shows an interaction between the C=C bond and a dithiole S atom (3.3 Å). The fact that the two dithiole rings are orthogonal in **3a** and **3b** precludes more than one alkyl chain from adopting the favorable all-staggered conformation. Thus, if both alkyl chains were supposed to

Table 1. Crystallograhpic data for **3a** and **3b**.

	3a	**3b**
Empirical formula	$C_{12}H_{14}S_{10}Zn$	$C_{16}H_{22}S_{10}Zn$
M [g·mol^{-1}]	544.20	600.31
T [K]	150(2) K	150(2)
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]	7.5896(5)	7.70290(10)
b [Å]	8.0138(6)	9.3494(2)
c [Å]	17.1292(15)	18.1802(4)
α [°]	87.400(3)	83.9880(10)
β [°]	80.111(3)	89.8730(10)
γ [°]	76.148(3)	65.7950(10)
V [Å^3]	996.49(13)	1186.42(4)
Z	2	2
D_x [g cm^{-3}]	1.814	1.680
μ [mm^{-1}]	2.273	1.918
F(000)	552	616
Crystal size [mm]	0.21 × 0.10 × 0.02	0.26 × 0.20 × 0.17
θ_{min} to θ_{max} [°]	3.55 to 25.49	3.76 to 27.48
Reflections collected/independent [R(int)]	17153/3694 [0.1847]	16596/5378 [0.0476]
T_{max}/T_{min}	0.952 and 0.652	0.721 and 0.611
Data/restraints/parameters	3694/ 6/208	5378/7/245
GoF on F^2	1.169	1.052
R_1 [$I > 2\sigma(I)$]	0.0983	0.057
wR_2 (all data)	0.2448	0.1562
$\Delta\rho_{max/min}$ [e·Å^{-3}]	1.109/–0.723	1.508/–1.472

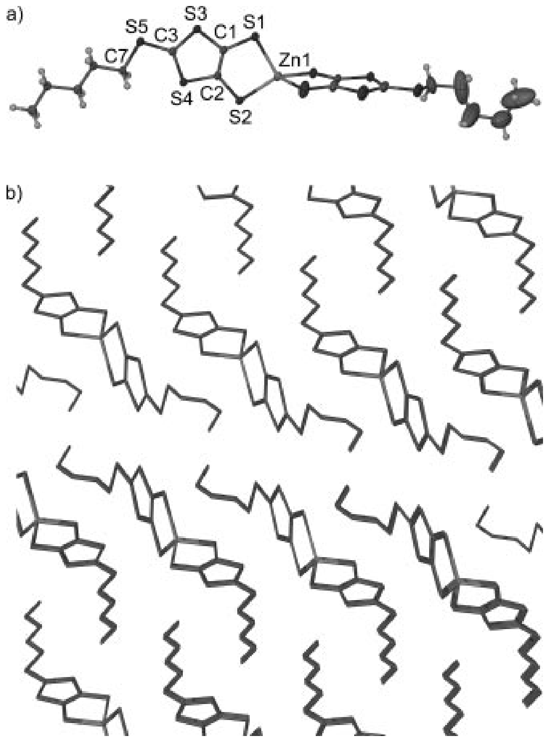


Figure 1. (a) Molecular structure of **3b** with the crystallographic numbering shown. (b) Packing of **3b** viewed along the *a* axis of the unit cell. Hydrogen atoms omitted for clarity.

Table 2. Average bond lengths [Å] for selected chemically equivalent bonds (a few chemically equivalent bonds do deviate more than 3 e.s.d.s). Data for $(Et_4N)_2[Zn(DMIT)_2]$ was taken from the literature.[20]

	3a	**3b**	$(Et_4N)_2[Zn(DMIT)_2]$ (**1**)
Zn(1)–S(1)	2.342(5)	2.3410(12)	2.345
S(1)–C(1)	1.724(16)	1.728(4)	1.735
C(1)–C(2)	1.42(2)	1.372(7)	1.362
C(1)–S(3)	1.722(16)	1.739(4)	1.753
S(3)–C(3)	1.707(16)	1.688(5)	1.721
C(3)–S(5)	1.701(16)	1.721(5)	1.661
S(5)–C(7)	1.811(17)	1.818(7)	

adopt a staggered conformation in the plane of their attached dithiole rings, one of them would penetrate into the next layer of molecules. Consequently, one of the alkyl chains is forced to twist to avoid such an unfavorable penetration. The molecule essentially makes the best of a bad lot. Only one alkyl chain can adopt the favorable all-staggered conformation and at the same time remain close packed. The other alkyl chain must then fend for itself without packing too loosely. This can apparently be done in a number of only slightly differing ways resulting in extensive disorder.

The absence of good hydrogen-bond donors (and hence of strong X–H···S hydrogen bond interactions) may account for the very different appearance of these compounds in the solid state (dark red) and in solution (dark blue).

NMR Investigations

A comparison of the ^{13}C NMR spectra recorded of compound **3c** with those recorded of $(Et_4N)_2[Zn(DMIT)_2]$ and 4,5-bis(hexylthio)-1,3-dithiole-2-thione (**4c**) reveal significant chemical shift differences for the resonances associated with the carbon atoms in the 1,3-dithiole moiety. The chemical shift values summarized in Table 3, suggest that the 1,3-

dithiole moiety gains some aromatic character upon alkylation of the thione functionality. This observation is also supported by the bond lengths listed in Table 2.

Table 3. Selected ^{13}C NMR spectroscopic data (δ values in ppm) for $(Et_4N)_2[Zn(DMIT)_2]$ (**1**), 4,5-bis(hexylthio)-1,3-dithiole-2-thione (**4c**), and **3c** at 298 K.

Compound	Solvent	C=C	S–C–S
$(Et_4N)_2[Zn(DMIT)_2]$ (**1**)	CD_3CN	136.4	210.2
4c	$CDCl_3$	136.5	211.6
3c	$CDCl_3$	158.5	168.5

Photophysical Investigations

The photophysical properties have been studied in $CHCl_3$ solutions at room temperature using absorption spectroscopy. The UV/Vis spectroscopic data of **3a**–**d** are listed in Table 4, together with those of $(Et_4N)_2[Zn(DMIT)_2]$ (**1**) and 4,5-bis(pentylthio)-1,3-dithiole-2-thione (**4b**). A comparison of the absorption spectra of **3b**, $(Et_4N)_2[Zn(DMIT)_2]$ (**1**), and 4,5-bis(pentylthio)-1,3-dithiole-2-thione (**4b**) is displayed in Figure 2.

Table 4. UV/Vis absorption band maxima (λ_{max}) and molar extinction coefficients (ε) for compounds **1**, **3a**–**d**, and 4,5-bis(pentylthio)-1,3-dithiole-2-thione (**4b**) in $CHCl_3$ at room temperature.

Compound	λ_{max} [nm] (ε [M^{-1} cm^{-1}])
$(Et_4N)_2[Zn(DMIT_2)]$ (**1**)	315 ($26\cdot10^3$), 494 ($21\cdot10^3$)
3a	308 ($20\cdot10^3$), 597 ($19\cdot10^3$)
3b	308 ($20\cdot10^3$), 598 ($19\cdot10^3$)
3c	308 ($21\cdot10^3$), 598 ($20\cdot10^3$)
3d	308 ($19\cdot10^3$), 598 ($19\cdot10^3$)
4b	278 ($6.4\cdot10^3$) 386 ($11\cdot10^3$)

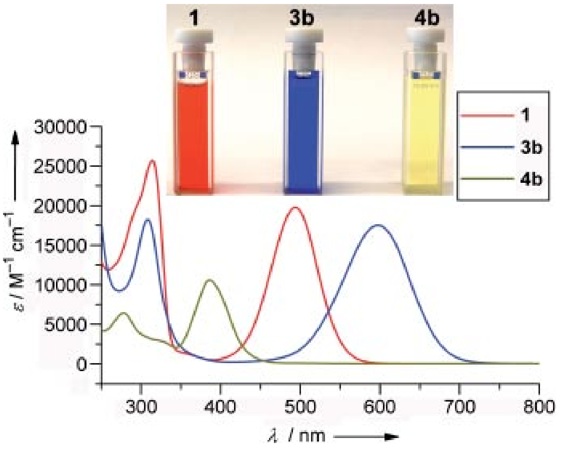


Figure 2. Absorption spectra recorded of $(Et_4N)_2[Zn(DMIT)_2]$ (**1**), **3b**, and 4,5-bis(pentylthio)-1,3-dithiole-2-thione (**4b**). The inset shows the actual color of the solutions of **1**, **3b**, and 4,5-bis(pentylthio)-1,3-dithiole-2-thione (**4b**).

The absorption spectrum of compound 4,5-bis(pentylthio)-1,3-dithiole-2-thione (**4b**) exhibits relative weak absorptions in the 250–450 nm region and no absorptions at $\lambda \geq 500$ nm, consistent with the observed pale yellow color (Figure 2, inset) of 4,5-bis(pentylthio)-1,3-dithiole-2-thione (**4b**) in $CHCl_3$. Dissolving $(Et_4N)_2[Zn(DMIT)_2]$ (**1**) in $CHCl_3$ produced a red solution (Figure 2, inset) with a concomitant strong absorption band being observed at λ_{max} = 494 nm ($\varepsilon = 21\cdot10^3\ M^{-1}\ cm^{-1}$) in the absorption spectrum, whereas a blue solution (Figure 2, inset) was obtained upon dissolving **3b** in $CHCl_3$. The absorption spectrum recorded of this blue solution of **3b** shows a strong absorption band centered at $\lambda_{max} \approx 598$ nm ($\varepsilon = 20\cdot10^3\ M^{-1}\ cm^{-1}$). This band can most likely be assigned to an intramolecular charge transfer (CT) taking place between the relative electron-rich thiolate groups and the 1,3-dithiolium moieties present in **3b**. To support this hypothesis, we carried out some molecular modeling calculations.[21] For simplicity, these investigations were conducted on **3a** which indicate that the two degenerated HOMO and HOMO–1 orbitals (Figure 3) mainly are located on the thiolate groups and the C=C bond, whereas the degenerated LUMO and LUMO+1 orbitals are located on the 1,3-dithiolium moieties. This led us to conclude that the Zn atom has only a minor contribution to the 598 nm absorption band. Instead, this absorption band can most likely be ascribed to an intramolecular electron transfer occurring between the thiolate groups and the 1,3-dithiolium moieties.

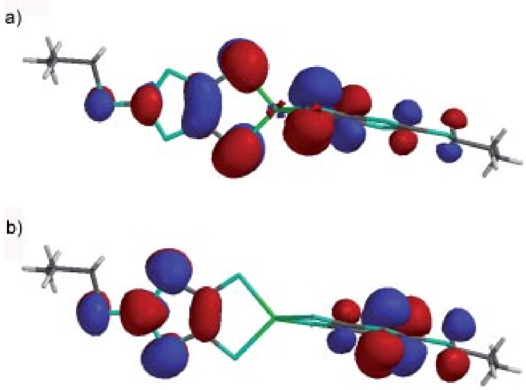


Figure 3. HOMO and LUMO orbitals of **3a**. (a) The degenerated HOMO and HOMO–1 orbitals are mainly located on the thiolate groups and the C=C bond, whereas (b) the degenerated LUMO and LUMO+1 orbitals are located on the 1,3-dithiolium moieties.

Conclusions

In conclusion, we have shown that alkylation of $(Et_4N)_2[Zn(DMIT)_2]$ (**1**) not only affords 4,5-bis(alkylthio)-1,3-dithiole-2-thiones **4**, but also takes place at the less nucleophilic thione functionalities producing a novel class of compounds **3** in which a Zn atom is coordinated to two aromatic 2-alkylthio-1,3-dithiolium-4,5-dithiolate moieties. Formation of **3** can be detected by the naked eye since solutions of $(Et_4N)_2[Zn(DMIT)_2]$ (**1**) and **3** display different colors, red and blue, respectively. Although the isolated yields of **3** generally were low, it seems that the formation of **3** is a common feature upon alkylation of $(Et_4N)_2[Zn(DMIT)_2]$

(**1**). Consequently, it can be expected that the method can be extended to produce more elaborate derivatives of **3**. The findings reported herein are undoubtedly not unimportant given the amount of research devoted to DMIT and its corresponding metal complexes.

Experimental Section

General Procedures: Chemicals and solvents were purchased from Aldrich and were used as received. Bis(tetraethylammonium) bis(2-thioxo-1,3-dithiole-4,5-dithiolato)zincate (**1**) was prepared according to a literature procedure.[13] Thin-layer chromatography (TLC) was carried out using aluminium sheets pre-coated with silica gel 60F (Merck 5554). The plates were inspected under UV light and, if required, developed in I_2 vapor. Column chromatography was carried out using silica gel 60F (Merck 9385, 0.040–0.063 mm). Melting points were determined with a Büchi melting point apparatus and are uncorrected. ^{1}H (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded at 298 K with a Gemini-300BB instrument, using tetramethylsilane (TMS) or the residual solvent as the internal standard. All chemical shifts are quoted on the δ scale, and all coupling constants (J) are expressed in Hertz (Hz). Samples were prepared using $CDCl_3$ or CD_3CN purchased from Cambridge Isotope Labs. High-resolution Fourier transform matrix-assisted laser-desorption/ionization mass spectrometry (HiRes-FT-MALDI-MS) was performed with an IonSpec 4.7 Tesla Ultima Fourier Transform mass spectrometer, utilizing a 2,5-dihydroxybenzoic acid (DHB) matrix. Infrared (IR) spectra were recorded with a Perkin–Elmer 580 spectrophotometer, while absorption spectra (UV/Vis) were recorded with a Shimadazu 1601 spectrophotometer. Elemental analyses were performed by the Atlantic Microlab, Inc., Atlanta, Georgia.

General Method for the Preparation of the Bis(2-alkylthio-1,3-dithiol-1-ium-4,5-dithiolato)zinc Compounds 3: Bis(tetraethylammonium) bis(2-thioxo-1,3-dithiole-4,5-dithiolato)zincate (**1**) (21.5 g, 30 mmol) was suspended in anhydrous MeCN (200 mL), whereupon the appropriate alkyl bromide (120 mmol) was added. The dark red reaction mixture was heated under reflux for 1 h until no more starting material could be detected by TLC analysis (R_f = 0.70; eluent: EtOAc/MeCN, 3:2). After being cooled to room temperature, the reaction mixture was concentrated in vacuo, and the resulting dark green oil was dissolved in CH_2Cl_2 and purified by column chromatography (750 mL of silica; diameter: 13.5 cm; eluent: CH_2Cl_2/petroleum ether, 1:9). The broad yellow band was collected, and the solvent evaporated to afford the 4,5-bis(alkylthio)-1,3-dithiole-2-thiones **4**. Thereafter, the eluent was changed to CH_2Cl_2 and a blue band was collected and concentrated to provide the title compounds **3a**–**c** as purple powders. Crystals suitable for X-ray analysis were prepared by diffusion of cyclohexane into $CHCl_3$ solutions of **3a** and **3b**, providing **3a** and **3b** as fine purple plates.

Bis(2-propylthio-1,3-dithiol-1-ium-4,5-dithiolato)zinc (3a): Yield: 46 mg (0.28 %); R_f = 0.45 (eluent: CH_2Cl_2); m.p.183–184 °C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.09 (t, J = 7.2 Hz, 6 H), 1.84 (sext, J = 7.2 Hz, 4 H), 3.18 (t, J = 7.2 Hz, 4 H). UV/Vis ($CHCl_3$): λ_{max} (ε) = 308 ($20\cdot10^3\ \text{M}^{-1}\ \text{cm}^{-1}$), 597 nm ($19\cdot10^3\ \text{M}^{-1}\ \text{cm}^{-1}$). IR (KBr): $\tilde{\nu}$ = 2960, 2923, 2866, 2013, 1363, 1285, 1013, 979, 906, 469 cm^{-1}. $C_{12}H_{14}S_{10}Zn$ (544.3): calcd. C 26.48, H 2.59, S 58.91; found C 26.15, H 2.55, S 58.39.

Bis(2-pentylthio-1,3-dithiol-1-ium-4,5-dithiolato)zinc (3b): Yield: 60 mg (0.33 %); R_f = 0.46 (eluent: CH_2Cl_2); m.p. 148.5–149.5 °C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.93 (t, J = 7.1 Hz, 6 H), 1.34–1.46 (m, 8 H), 1.80 (q, J = 7.4 Hz, 4 H), 3.20 (t, J = 7.4 Hz, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 22.2, 28.2, 30.8, 40.4, 158.8 (one line for the trithiocarbonate carbon atom is missing). UV/Vis ($CHCl_3$): λ_{max} (ε) = 308 ($20\cdot10^3\ \text{M}^{-1}\ \text{cm}^{-1}$), 598 nm ($19\cdot10^3\ \text{M}^{-1}\ \text{cm}^{-1}$). IR (KBr): $\tilde{\nu}$ = 2946, 2925, 2854, 2008, 1453, 1424, 1349, 1022, 903, 730, 467 cm^{-1}. HiRes-FT-MALDI-MS: calcd. for $C_{16}H_{22}S_{10}Zn$ [$M^{+\cdot}$] 597.8215; found: 597.8209. $C_{16}H_{22}S_{10}Zn$ (600.4): calcd. C 32.01, H 3.69, S 53.41; found C 32.01, H 3.60, S 53.60.

Bis(2-hexylthio-1,3-dithiol-1-ium-4,5-dithiolato)zinc (3c): Yield: 75 mg (0.49 %); R_f = 0.45 (eluent: CH_2Cl_2); m.p. 161.5–163.0 °C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, J = 6.7 Hz, 6 H), 1.25–1.50 (m, 12 H), 1.79 (q, J = 7.4 Hz, 4 H), 3.20 (t, J = 7.4 Hz, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 22.6, 28.3, 28.5, 31.2, 40.4, 158.5, 168.5 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (ε) = 308 ($21\cdot10^3\ \text{M}^{-1}\ \text{cm}^{-1}$), 598 nm ($20\cdot10^3\ \text{M}^{-1}\ \text{cm}^{-1}$). IR (KBr): $\tilde{\nu}$ = 2946, 2922, 2851, 2006, 1462, 1421, 1357, 1009, 904, 725, 465 cm^{-1}. HiRes-FT-MALDI-MS: calcd. for $C_{18}H_{26}S_{10}Zn$ [$M^{+\cdot}$] 625.8528; found 625.8522. $C_{18}H_{26}S_{10}Zn$ (628.4): calcd. C 34.40, H 4.17, S 51.02; found C 34.38 H 4.29, S 51.31.

Bis(2-ethylthio-1,3-dithiol-1-ium-4,5-dithiolato)zinc (3d): Bis(tetraethylammonium) bis(2-thioxo-1,3-dithiol-1-ylium-4,5-dithiolato)-zincat (**1**) (21.5 g, 30 mmol) was suspended in MeCN (200 mL), whereupon triethyloxonium tetraflouroborate (25.0 g, 120 mmol) was added. The dark red reaction mixture was heated under reflux for 5 min until no more starting material could be detected by TLC analysis (R_f = 0.70; eluent: EtOAc/MeCN, 3:2). The reaction mixture was cooled to room temperature and concentrated in vacuo. The resulting dark red oil was dissolved in CH_2Cl_2. Column chromatography (800 mL of silica; diameter: 13.5 cm; eluent: CH_2Cl_2/petroleum ether, 1:4) gave a yellow band and a red band which was discarded. The bis(2-ethylthio-1,3-dithiol-1-ium-4,5-dithiolato)zinc (**3d**) was then eluted as a blue band with CH_2Cl_2. Removal of the solvent provided the title compound **3d** as a purple microcrystalline powder. Yield: 169 mg (1.1 %); R_f = 0.20 (eluent: CH_2Cl_2); m.p. 164.0–165.0 °C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.49 (t, J = 7.4 Hz, 6 H), 3.22 (q, J = 7.4 Hz, 4 H). UV/Vis ($CHCl_3$): λ_{max} (ε) = 308 ($19\cdot10^3\ \text{M}^{-1}\ \text{cm}^{-1}$), 598 nm ($19\cdot10^3\ \text{M}^{-1}\ \text{cm}^{-1}$). IR (KBr): $\tilde{\nu}$ = 2923, 2011, 1445, 1348, 1288, 1262, 1061, 1016, 905, 787, 466 cm^{-1}. HiRes-FT-MALDI-MS: $C_{10}H_{10}S_{10}Zn$ [$M^{+\cdot}$]: calcd. 513.7276; found 513.7265. $C_{10}H_{10}S_{10}Zn$ (516.23): calcd. C 23.27, H 1.95, S 62.11; found C 23.36, H 1.89, S 62.30.

X-ray Crystallography: Details are listed in Table 1. CCDC-601004 (**3a**) and -601005 (**3b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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