SHORT PAPER

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A novel derivative of hexathiocane having the 4,5-dimethylthio-1,3-dithiol-2-ylidene moiety[†]

Jie Dai,[a]* Min-Yan Zhou[a], Guo-Qing Bian[a], Xin Wang[a], Qing-Feng[a], Xu, Megumu[a] Munakata[b] and Masahiko Maekawa[b]

[a]*Department of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215006, P.R.China*
[b]*Department of Chemistry, Kinki University, Kowakae, Higashi-Osaka 577-8502, Japan*

An unexpected reaction forming 4,8-bis(4,5-dimethylthio-1,3-dithiol-2-ylidene)-1,2,3,5,6,7-hexathiocane is described.

Keywords: 1,2,3,5,6,7-hexathiocanes, 1,3-dithioles, crystal structures, medium-ring compounds, polysulfur rings

Unlike oxygen, sulfur can form relatively stable polyatomic structures $(\text{-S-})_n$ due to the effective overlap of its valence orbitals and low interatomic repulsion. A series of cyclic molecules of sulfur with 6–20 members have been confirmed by crystal structure determination,[1] in which the most stable ring at room temperature is the eight-membered S_8 molecule. A number of heterocyclic S_8 analogs, such as $N_2H_2S_6$ (Fig. 1) and $N_4H_4S_4$, have been reported,[2] while analogs with a C_2S_6 ring are uncommon. Franz *et al*. have synthesised 1,2,3,5,6,7-hexathiocane by treating $CH_2(SH)_2$ with SCl_2.[3] Herein we report an unusual reaction for the synthesis of a new compound, 4,8-bis(4,5-dimethylthio-1,3-dithiol-2-ylidene)-1,2,3,5,6,7-hexathiocane (**5**, Fig. 1). The reaction was found during a study of metal complexes of sulfur-rich ligands. To our knowledge few or no examples with a C_2S_6 ring have been characterised by crystal structure. This compound will also be interesting for synthetic scientists exploring derivatives of tetrathiafulvalene (TTF).

The goal of our study is new TTF-based or 2-thione-1,3-dithiole-4,5-dithiolate (DMIT) based complexes. It is well known that these compounds exhibit useful electrical, magnetic and optical properties.[4] Recently a new type of protected dithiolate ligand $[(RS)_2TTF(SCH_2CH_2CN)_2]$ (**1**) has received much attention, since selective sequential deprotection and alkylation of a preformed 1 is possible (Scheme 1).[5]

Up to now, a number of metal complexes of bis-deprotected ligands **1** have been reported.[6] We have synthesised for the first time a tetranuclear complex $[Me_4N]_2[Cu_4(S_2TTF\ (SMe)_2)_3]$.[7] On the other hand, metal complexes with mono-deprotected or mono-functional thiolate ligands of this type have been isolated only as the caesium salt $[(MeOOC)_2TTF(COOMe)(SCs)]$.[5] To exploit this type of complex we synthesised a mono-functional derivative of TTF, 2-(2-cyanoethylthio)-3,6,7-tri(methylthio)tetrathiafulvalene (**3**).[5] By reacting mono-deprotected **3** (namely **4**) with nickel dichloride hydrate in THF (see discussion following), the solution turned brown; then the filtrate was set aside overnight and open to the atmosphere. Unexpectedly, crystals of **5** were isolated, which included a C_2S_6 eight-membered ring and two segments of TTF moiety. Details of the preparation are given in the experimental section. Scheme 2 shows the synthetic route.

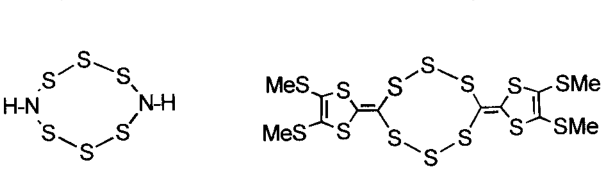
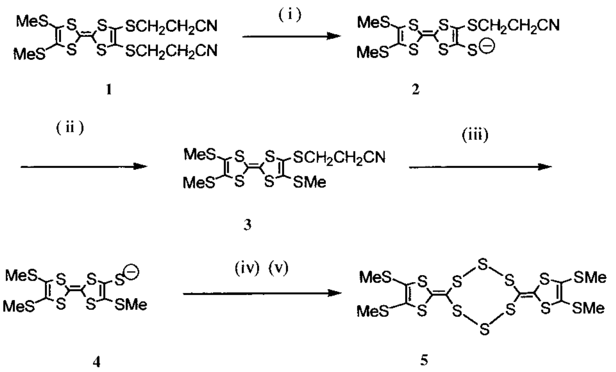
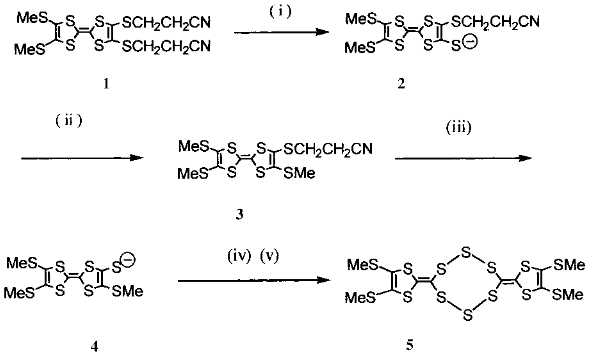

$N_2H_2S_6$ **5**

Fig. 1 Molecular structure of Compound 5 and $N_2H_2S_6$.



Scheme 1 Selective sequential deprotection of **1**. (i) THF/1 equiv. of CsOH in methanol; (ii) MeI; (iii) Me4NOH in methanol; (iv) $NiCl_2$ $6H_2O$; (v) overnight open to air.

Compound **5** forms air-stable red prisms and can be prepared in good yield (about 54% calculated from **3**). An ORTEP view of the structure[8] is shown in Fig. 2. The centre of the compound is an eight-membered C_2S_6 ring in analogy to the S_8 crown molecule. Since C(1) and C(7) (corresponding to positions 4 and 8 respectively in the ring nomenclature),are sp^2-hybridised their bond angles S–C–S in the ring are 120.2(3)° and 120.6(2)° respectively, in contrast to the sulfur atoms that are sp^3 hybrids and have bond angle ranging from 105.4° to 107.9°.



Scheme 2 The synthetic path for compound **5**.

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* To receive any correspondence. E-mail: daijie@suda.edu.cn

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

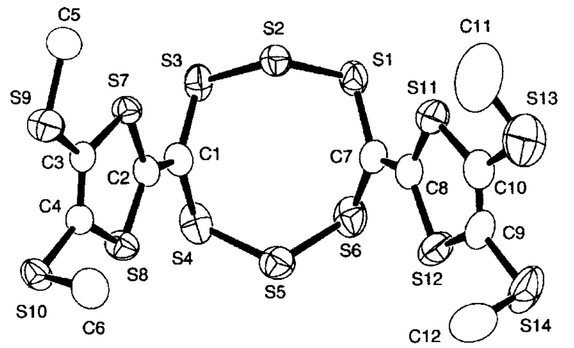

Fig. 2 ORTEP view of the compound 5. Selected bond lengths (Å) and angles (deg): S(1)–S(2) 2.062(2), S(2)–S(3) 2.063(2), S(3)–C(1) 1.748(4), C(1)–C(2) S(1)–C(7)–S(6) 120.2(3), S(2)–S(1)–C(7) 105.8(1), S(1)–S(2)–S(3) 105.4.

The compound **5** is assembled from two $C_6H_6S_6$ moieties by inserting sulfur atoms S(2) and S(5). In profile, the molecule resembles a crab and shows a pseudo-C_{2v} symmetric structure. Intermolecular S···S contacts shorter than the van der Waals distance of S···S (3.60 Å) are found in this compound: S(4)–S(9) 3.464(2), S(9)–S(9) 3.493(2), S(4)–S(14) 3.518(2) and S(3)–S(10) 3.569(1). No intramolecular contact was found between S(2) and S(5). Franz *et al*. has proposed the existence of the intramolecular contact in analog of $C_2H_4S_6$ and that divides the eight-member cycle to two fused pentcyclic strcture.[3]

The resulting product **5** was completely different from our expected complex [Ni(S(MeS)TTF(SMe)$_2$)$_2$] ((MeS)$_2$TTF (SMe)S, **4**, Scheme 2). Repeated experiments consistently gave good yields of product **5**. While the mechanism of the reaction is in doubt, we found the compound cannot be obtained from freshly-distilled THF solvent. Thus two factors may be concerned with this reaction: one is the presence of water, and the other is the trace of peroxide contained in the solvent if the THF is not freshly distilled (positive iodide test).[9] The first factor was ruled out by adding a trace of H_2O to the dry THF in the experiment. Therefore the peroxide might be required to break down the mono-deprotected anion **4**. The synthetic reaction was under argon atmosphere, while the filtrate was open to the air overnight. If the solution was sealed in a glass tube, no product **5** formed. Although some other efforts were made to reveal the mechanism, the reaction is complicated and still unclear. However, a nickel(II) induced decomposition is believed to occur. Then a sulfur insertion occurs between $C_6H_6S_6^{2-}$ dithiolate moieties (half of the compound except S(2) and S(5)) and loose S or S^{2-}. The existence of a di-anionic intermediate is supported by the reported preparation of 1,2,3,5,6,7-hexathiocane $C_2H_4S_6$, which is synthesized by treating $CH_2(SH)_2$ with SCl_2.[3]

To confirm the action of the nickel, instead of the nickel dichloride diacetonitrile-palladium(II) dichloride was selected in the reaction using the same solvent and conditions. However, in contrast to the nickel salt, the expected mononuclear complex [Pd(S(MeS)TTF(SMe) $_2$)] (**6**) precipitated immediately. Its insolubility may be the reason for its resistance to degradation.

In conclusion, a novel compound (**5**) having a C_2S_6 eight-membered ring has been synthesised in good yield. Preliminary experiments have shown that nickel chloride and oxidation are necessary in the preparation. However, the details of the mechanism require further study.

Experimental

All the syntheses were carried out under Ar using the Schlenk technique, except where indicated. Diffraction data were collected on a Rigaku AFC-5R diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å) and a rotating anode generator. A total of 5742 reflections were collected using the ω-2θ scan technique within a 2θ range 55.0°, in which 5451 were unique. An empirical absorption correction based on azimuthal scans of several reflections was applied. The structure was solved by direct methods (SIR97) and expanded using Fourier techniques (DIRDIF94). The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 3140 reflections [$I > 2\sigma(I)$]. All crystallographic computations were performed by using the teXsan program system. The crystallographic data are reported in reference 8.

2-(2-Cyanoethylthio)-3,6,7-tris(methylthio)tetrathiafulvalene (**3**): The precursor **3** was prepared in similar manner as described.[5] Instead of DMF, THF was used as the solvent. Thus when the idomethane was added, CsI salt precipitated in the THF solution and was discarded. The crude product was purified by column chromatography (silica gel, CH_2Cl_2), to give **3** as an analytically pure compound.

^{1}H NMR ($CDCl_3$/TMS): δ = 3.03 (t, 2H), 2.71 (t, 2H), 2.45 (s, 9H).

IR (KBr): δ (cm^{-1}) = 2917s, 2245m, 1501s, 1431s, 1420s, 1285m, 972m, 957s, 902vs, 772s.

Anal. Calc. for $C_{12}H_{13}NS_8$: C, 33.72; H, 3.04; N, 3.28. Found: C, 33.48; H, 3.35; N, 2.94 %.

4,8-Bis (4,5-dimethylthio-1,3-dithol-2-ylidene)-1,2,3,5,6,7-hexathiocane (**5**): To a solution of **3** (63.9 mg, 0.15 mmol) in degassed THF (6 ml, positive peroxide test), was added Me_4NOH in methanol, and the orange solution changed colour to reddish colour. Then $NiCl_2 \cdot 6H_2O$ (18 mg, 0.075 mmol) was added, whereupon the solution turned brown and a green-greyish precipitate formed. The mixture was stirred for 60 min under Ar and the precipitant was filtered off. The brown filtrate was laid aside overnight open to the air. The resulting product was obtained as red crystals, yield: 25 mg (yield 54%), m.p. 108–110 °C. A sample suitable for X-ray structure determination in a sealed glass tube was obtained by re-crystallisation from chloroform.

^{1}H NMR ($CDCl_3$/TMS): δ = 2.47 (s, 12H)

^{13}C NMR ($CDCl_3$/TMS): δ = 172.2, 132.1, 19.1

IR (KBr): ν (cm^{-1}) = 2991w, 2913m, 1411vs, 1313w, 964m 876w, 769m.

Anal. Calc. for $C_{12}H_{12}S_{14}$: C, 23.82; H, 2.00. Found: C, 24.12; H, 2.20 %.

Bis(2-mercapto-3,6,7-tri(methylthio)tetrathiafulvalene) palladium(II) (**6**): To a solution of **3** (21.4 mg, 0.05 mmol) in degassed THF (6 ml), was added Me_4NOH in methanol. The orange solution changed colour to red. Then Pd(CH_3CN)$_2$Cl$_2$ (6.5 mg, 0.025 mmol) was added and the solution turned dark and a black precipitate formed. The filtrated precipitate was washed with methanol and dried *in vacuo* (10.3 mg, 48%). It is insoluble in ordinary solvents, and decomposes on heating.

IR (KBr) ν (cm^{-1}): 2914w, 1500m, 1417s, 1308w, 1004m, 966m, 899vs, 768s.

Anal. Calc. for $C_{18}H_{18}PdS_{16}$: C, 25.35; H, 2.11. Found: C, 25.34; H, 2.51 %.

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8 Crystallographic data for **5**: $C_{12}H_{12}S_{14}$, M=605.07, triclinic, *P*-1, *a* =10.645(1) Å, *b* = 11.486(1) Å, *c* = 10.274(1) Å, α = 99.654(8)°, β = 106.457(8)°γ = 90.088(10)°, *V* =1186.1(2) Å^3, *Z* =2, *D* (calc.)= 1.649 g cm^{-3}, R_1 =0.043, Goodness of fit 1.16. Further details are available on request from the Director of the Cambridge Crystallographic Data Centre (No. CCDC-152550), 12 Union Road, Cambridge CB2 1EZ, UK (deposit@ccdc.cam.ac.uk).

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