Synthesis and Crystal Structure of [Fe(C_5H_4)$_2$$S_3$O]: The First Organometallic Trisulfane Oxide

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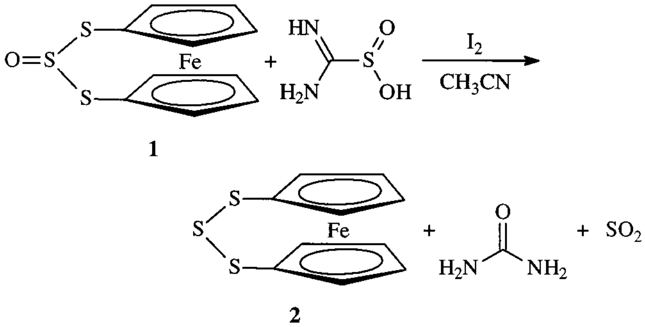
Summary: The reaction of 1,1′-ferrocenylene dithiol with thionyl chloride and pyridine at 20 °C yields 1,1′-(1,2,3-trithia[3])ferrocenophane-2-oxide ***1****, which can easily be reduced to the corresponding trisulfane.*

1,1′-Dithia-substituted ferrocenes[1] have recently received much attention, either as open-chain derivatives[2] or as ferrocenophanes.[3] Of the latter, the 1,2,3-trithia[3]ferrocenophane **2** has been studied most extensively, but even the [1]ferrocenophane with a single sulfur atom as a bridge has been prepared and structurally characterized.[4] Ring-opening polymerization of such compounds yields interesting organometallic polymers.[5] Organic trisulfane-2-oxides of type R−S−S(O)−S−R are known with various bulky organic substituents,[6] while the related sulfur oxyacid H−S−S(O)−S−H and derivatives with small alkyl groups are unstable and therefore unknown as pure materials. However, the structures of $(HS)_2SO$ and $(MeS)_2SO$ have been elucidated by *ab initio* MO calculations.[6a,7] The unsubstituted trisulfane-2-oxide is believed to play a major role as an intermediate in the industrial Claus reaction between H_2S and SO_2 for the production of elemental sulfur.[7] The only metal-containing polysulfane oxides with more than two neighboring sulfur atoms are the pentasulfane-3-oxide of titanocene [$(C_5H_5)_2TiS_5O$][8] and the platinum compound [$(Ph_3P)_2PtS_3O$];[9] only the latter has been structurally investigated.

We have now prepared the first ferrocenylene trisulfane oxide by reaction of the 1,1′-dithiol of ferrocene with thionyl chloride at 20 °C in carbon disulfide in the presence of pyridine. The dark red crystals of the 1,1′-(1,2,3-trithia[3])ferrocenophane-2-oxide **1** are air-stable at 20 °C and are very well soluble in benzene, CH_2Cl_2, $CHCl_3$, CS_2, and THF. On melting (mp 121 °C) the sample slowly decomposes to an insoluble product without SO_2 evolution, in sharp contrast to the behavior of other organic trisulfane-2-oxides. However, the EI mass spectrum exhibits the molecular ion with high intensity at a sample temperature of 105 °C. Another characteristic feature is the strong IR absorption of the solid at 1098 cm^{-1} originating from the SO stretching mode.

The thermal stability of **1** together with the rigidity of the S_3O group opens the possibility for derivatization reactions at the SO bond. For example, reduction of **1** with aminoiminomethane sulfinic acid yielded the trisulfane **2** in 86% yield:



Attempts to oxidize **2** by trifluoroperoxoacetic acid to **1** failed.

The structure of **1** in the solid state was determined by single-crystal X-ray diffraction. The molecular structure is depicted in Figure 1. The molecular symmetry is approximately C_s, although the molecules occupy general positions. The two cyclopentadienyl rings are practically eclipsed and almost parallel (interplanar angle 2.5(1)°, opening up toward the S_3 bridge). The same conformation has been observed in crystalline **2**.[10] The trisulfane-2-oxide unit C−S−S(O)−S−C has a *syn* conformation with the torsion angle C(4)−S(3)−S(2)−S(1) = −66.08(6)°. For the free acid $(HS)_2SO$[7] and the dimethyl derivative[6a] this conformation was calculated to be slightly less stable than the less symmetrical form with one X−S−S−S torsion angle close to 180° (X = C or H). The torsion angle C(4)−S(3)−S(2)−O amounts to +48.91(9)°. The S−S bond lengths are almost identical to those in most other organic trisulfane-2-oxides,[6a] and the same holds for the S=O distance. As in other cyclic

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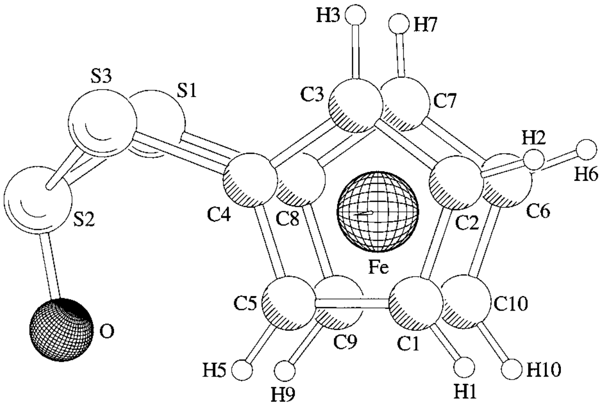

Figure 1. Molecular structure of **1** in the crystal. Selected internuclear distances (Å) and angles (deg): S(1)−S(2) = 2.1180(7), S(2)−S(3) = 2.1297(7), S(2)−O = 1.463(2), S(1)−C(8) = 1.752(2), S(3)−C(4) = 1.746(2), S(1)−S(2)−S(3) = 104.22(3), S(1)−S(2)−O = 108.24(7), S(3)−S(2)−O = 108.12(7), C(8)−S(1)−S(2) = 106.04(6), C(4)−S(3)−S(2) = 105.21(5).

sulfane oxides,[11] the oxygen atom is in an axial position, probably as a result of the anomeric effect. There is no indication from the solution NMR spectra that the conformer with the O atom in the equatorial position exists in equilibrium with **1**. In the structure of **1** there are neither intramolecular nor intermolecular close contacts between iron and oxygen atoms (smallest Fe···O distance intramolecularly 3.750(2) Å, intermolecularly 5.233 Å). The shortest intermolecular distance between sulfur and oxygen atoms is 5.80(1) Å, far beyond the van der Waals distance.

Experimental Section

The initial reaction was performed under an atmosphere of dry nitrogen. Solvents were dried and distilled before use.

To ferrocenylene dithiol (1.0 mmol) and pyridine (2.0 mmol) in dry carbon disulfide (30 mL) was added thionyl chloride (1.0 mmol) using a syringe. After stirring for 15 min the precipitated py·HCl was filtered off and the solution cooled to −25 °C for 12 h. The cold solution was filtered, the solvent volume reduced at 20 °C by ca. 50%, and the solution cooled to −25 °C again. The residual py·HCl was filtered off, and *n*-hexane was added to the filtrate until a slight turbidity occurred. This mixture was cooled to −25 °C, whereupon **1** crystallized as a red solid (yield 56%); mp 121 °C (dec).

Anal. Calcd for $C_{10}H_8FeOS_3$ (296.19): C, 40.55; H, 2.72; S, 32.47. Found: C, 40.71; H, 2.68; S, 32.67. MS (EI; *m*/*z*, ion, relative intensity (%)): 296, M^+ (100); 280 [$M^+ - O$] (23); 248, [$M^+ - SO$] (99); 184, [$(C_5H_4)_2Fe^+$] (23); 152, [$(C_5H_4S)Fe^+$] (29); 96, [S_3^+] (13); 56, Fe^+ (25). ^1H NMR (200 MHz, CD_2Cl_2, 25 °C): δ 4.11 (m, 2H), 4.28 (m, 2H), 4.56 (m, 4H). ^{13}C NMR (200 MHz, CD_2Cl_2, 25 °C): δ 68.14; 70.88; 73.05; 74.45; 77.66.

The thermal decomposition was studied both in a conventional melting point determination apparatus (heating to 140 °C) and using a differential scanning calorimetry apparatus. The melting process was irreversible due to polymerization of the sample, as indicated by the insolubility in methylene chloride. When **1** (0.33 mmol), aminoiminomethane sulfinic acid[12] (0.66 mmol) and traces of iodine were refluxed in acetonitrile (10 mL) for 1 h, SO_2 was produced. The cooled (20 °C) solution was filtered, the precipitate of urea was washed with MTB ether, and the organic phases were combined. After evaporation of the solvents, the residue was dissolved in MTB ether. The organic phase was first washed with aqueous sodium thiosulfate followed by water and dried over magnesium sulfate. After evaporation of the solvent **2** was isolated in 86% yield (identified by CH analysis, mp, IR, MS, Raman, ^1H NMR spectra as compared to an authentic sample).

Table 1. Crystal Data, Data Collection, and Structure Refinement for 1

formula	$C_{10}H_8FeOS_3$
fw	296.19
color	red
cryst size, mm	0.3 × 0.15 × 0.6
cryst syst	monoclinic
space group	$P2_1/n$
temp, K	293(2)
wavelength, Å	0.71069
a, Å	7.3957(2)
b, Å	13.7751(4)
c, Å	10.6106(3)
α, deg	90
β, deg	99.4040(10)
γ, deg	90
V, $Å^3$	1066.44(5)
Z	4
density (calcd), g cm^{-1}	1.845
abs coeff, mm^{-1}	1.965
F(000)	600
scan range, deg	$2.44 \le \theta \le 38.59$
no. of reflns collected	14634
no .of ind reflns	5830 ($R_{int} = 0.0623$)
refinement method	full-matrix least-squares on F^2
no of data/restraints/params	5828/0/169
goodness-of-fit on F^2	0.949
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0448, wR2 = 0.0989
R indices (all data)	R1 = 0.0684, wR2 = 0.1214
largest diff peak and hole, e $Å^{-3}$	0.791, −1.027

X-ray Crystallography. The details of the crystal structure determination and refinement are given in Table 1. Data were collected on a Siemens Smart CCD diffractrometer using Mo Kα radiation ($\lambda = 0.71069$ Å). The structure was solved after *Lp* and absorption correction (SADABS[13]) by direct methods (SHELXS[14]) and refined with anisotropic thermal parameters for the non-hydrogen atoms (SHELXL[15]). Hydrogen positions were refined with a riding model. The drawing was created with the DIAMOND[16] program.

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Supporting Information Available: Tables of crystal data and structure refinement details, atom coordinates, internuclear distances, bond angles, and thermal parameters as well as an ORTEP drawing of **1**.[17] This material is available free of charge via the Internet at http://pubs.acs.org.

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