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Oxidation Products of 1,2,3-Trithia[3]ferrocenophane: Structures of the Corresponding Sulfoxide and Sulfone

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*Summary: Oxidation of 1,2,3-trithia[3]ferrocenophane **1** by 3-chloroperoxobenzoic acid at 25 °C in dichloromethane yields the corresponding sulfoxide **2** and the sulfone **3** depending on the molar ratio. The oxidation takes place at one of the terminal sulfur atoms exclusively; the remarkably stable trisulfane-1-oxide **2** can easily be reduced to the trisulfane **1**.*

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 **1** 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] In an attempt to prepare novel oxides of ferrocene trisulfane by oxidation of **1** with 3-chloroperoxobenzoic acid (mCPBA) at 25 °C, we obtained the 1,1′-(1,2,3-trithia[3])ferrocenophane-1-oxide **2** in 74% yield and the 1,1′-(1,2,3-trithia[3])ferrocenophane-1,1-dioxide **3** in 60% yield.[6]

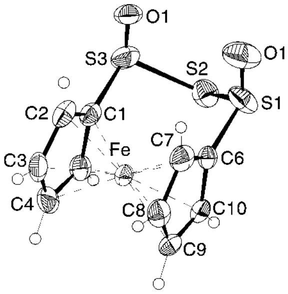

Figure 1. Molecular structure of **2** in the crystal. The positions O(1) and O(1′) are disordered (approximately in the ratio 55:45%). Thermal ellipsoids with 50% probability. Selected internuclear distances (Å) and angles (deg.): S(1)−S(2) = 2.0722(18), S(2)−S(3) = 2.1290(17), S(3)−O(1) = 1.383(6), S(1)−O(1′) = 1.338(8), S(1)−C(6) = 1.755(4), S(3)−C(1) = 1.763(4), S(1)−S(2)-S(3) = 102.76(8), S(2)−S(1)−O(1′) = 118.0(4), S(2)−S(3)−O(1) = 113.4(3), C(1)−S(3)−S(2) = 101.49(14), C(6)−S(1)−S(2) = 101.98(14).

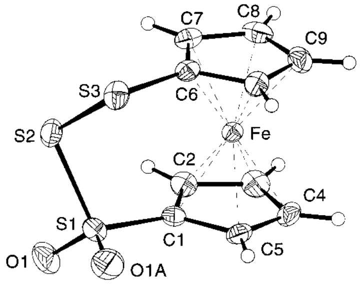

Figure 2. Molecular structure of **3** in the crystal (thermal ellipsoids with 50% probability). Selected internuclear distances (Å) and angles (deg.): S(1)−S(2) = 2.1168(11), S(2)−S(3) = 2.0305(11), S(1)−O(1) = 1.443(2), S(1)−O(1A) = 1.430(3), C(1)−S(1) = 1.743(3), C(6)−S(3) = 1.764(3), S(1)−S(2)−S(3) = 101.79(4), S(2)−S(1)−O(1) = 101.85(13), S(2)−S(1)−O(1A) = 110.28(13), C(1)−S(1)−S(2) = 106.92(9), C(6)−S(3)−S(2) = 101.60(9).

The sulfoxide **2** is an isomer of 1,1′-(1,2,3-trithia[3])ferrocenophane-2-oxide **4**, which we had prepared previously by reaction of 1,1′-ferrocenylene dithiol with thionyl chloride and pyridine at 25 °C.[7] The red air-stable crystals of **2** decompose above 130 °C without melting. The EI mass spectrum exhibits the molecular ion with high intensity at a sample temperature of 128 °C. Another characteristic feature is the strong IR absorption of the solid at 1090 cm^{-1} originating from the SO stretching mode. Reduction of **2** by aminoiminomethane sulfinic acid yielded the trisulfane **1** in 94% yield.

Heating of **2** in toluene to 111 °C for 3 min did not result in decomposition; however, after refluxing for 1 h most of the sample had decomposed. The structure of **2** in the solid state was determined by single-crystal X-ray diffraction. The molecular structure is depicted in Figure 1. The oxygen atom of **2** is linked to one of the terminal sulfur atoms but is disordered and occupies the position O1 and O1′ approximately in a 1:1 ratio. As a consequence of this disorder, the molecular parameters of the S_3O unit have to be critically analyzed. The SO bond lengths of 1.38 and 1.36 Å are considerably

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[1] Review on substituted ferrocenes: Herberhold, M. In *Ferrocenes*; Togni, A., Hayashi, T., Eds.; VCH: Weinheim, 1995; Chapter 5.

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[3] (a) Takemoto, S.; Kuwata, S.; Nishibayashi, Y.; Hidai, M. *Inorg. Chem.* **1998**, *37*, 6428. (b) Johnston, E. R.; Brandt, P. F. *Organometallics* **1998**, *17*, 1460. (c) Brandt, P. F.; Compton, D. L.; Rauchfuss, T. B. *Organometallics* **1998**, *17*, 2702. (d) Compton, D. L.; Rauchfuss, T. B. *Organometallics* **1994**, *13*, 4367. (e) Gibson, V. C.; Long, N. J.; Martin, J.; Solan, G. A.; Stichbury, J. C. *J. Organomet. Chem.* **1999**, *590*, 115.

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[6] The oxidation of polysulfido ligands in metallocene complexes has been reported before: Cp_2MoS_2O and Cp_2MoS_4O were obtained by oxidation of Cp_2MoS_2 and Cp_2MoS_4 by mCPBA.; see: Rys, A. Z.; Lebuis, A.-M.; Shaver, A.; Harpp, D. N. *Organometallics* **1999**, *18*, 1113. However, in these compounds the sulfur atoms are coordinated to the metal atom.

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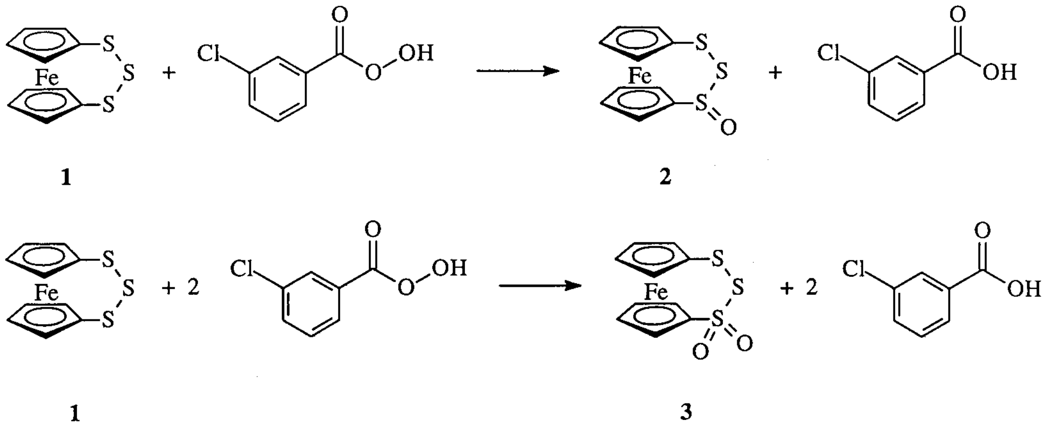
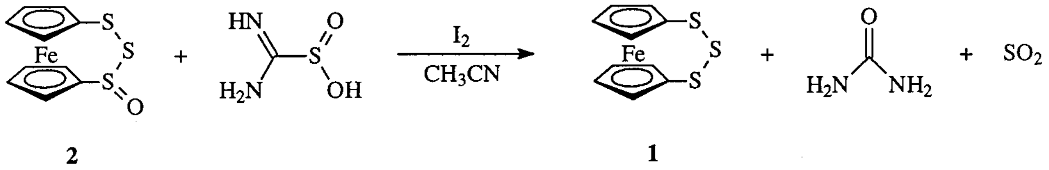
Scheme 1



Scheme 2



shorter than in the isomeric trisulfane-2-oxide **4** (1.463 Å) and in the sulfone **3** (1.430 and 1.443 Å; see below). On the other hand, the two SS bonds of **2** show bond lengths (2.116 and 2.077 Å) that are quite normal for sulfane oxides of this type. For example, the SS bonds of **4** are of lengths 2.118 and 2.130 Å. The ferrocene trisulfane unit fcS_3 of **2** exhibits about the same conformation as in crystalline **1**[8] with the two cyclopentadienyl rings practically eclipsed. The dihedral angle between the two cyclopentadienyl rings is 2.7° (opening toward the S_3 bridge), and the angle Z−Fe−Z′ at the iron atom between the two ring centers is 177.1(3)°. The remaining bond distances, bond angles, and torsion angles are all found in the normal range. There are no close contacts shorter than 3.96 Å between the oxygen and iron atoms in **2**, neither intra- nor intermolecularly.

The sulfone **3** was prepared by oxidation of either **1** or **2** with mCPBA in dichloromethane at 25 °C. The red crystals obtained decompose above 140 °C without melting. The EI mass spectrum exhibits the molecular ion with 100% intensity. The symmetric and asymmetric SO stretching vibrations give rise to two very strong IR absorptions at 1111 and 1310 cm^{-1}, and the OSO bending vibrations yield another strong band at 640 cm^{-1}. The structure of **3** in the solid state was determined by single-crystal X-ray diffraction. The molecular structure is depicted in Figure 2. Both oxygen atoms are linked to the same terminal sulfur atom with SO bond lengths of 1.430 and 1.443 Å, which are typical values for sulfones. The adjacent SS bond is of length 2.117 Å, while the other SS bond is shorter (2.031 Å), as expected.[9] Otherwise, the structure is similar to those of **2** and **4**. The dihedral angle between the two cyclopentadienyl rings is 1.1° (opening toward the S_3 bridge), and the angle Z−Fe−Z′ at the iron atom between the two ring centers is 178.6(2)°.

The ^1H NMR spectra of compounds **1**−**4** are quite different (see below) and allow the rapid identification of each species in solution. As far as the relative thermodynamic stability of the isomers **2** and **4** is concerned, one can only refer to certain model compounds that have been investigated by high-level ab initio MO calculations. The energy of the hypothetical acid H−S(=O)-S−S−H was calculated as 31 kJ mol^{-1} higher than that of the isomer H−S−S(=O)−S−H.[10] The reverse order of stabilities has been found for the most stable conformations of the two methyl derivatives Me−S(=O)−S−S−Me and Me−S−S(=O)−S−Me: the former is 11 kJ mol^{-1} more stable than latter.[11] Therefore, we conclude that **2** will be more stable thermodynamically than **4** and that **2** is consequently not expected to convert to **4** on heating. Generally, open-chain trisulfane-1-oxides are thermally rather unstable and often decompose slowly at room temperature to mixtures of sulfanes, sulfane oxides (sulfoxides), and sulfane dioxides (sulfones).[12] Cyclic trisulfane monoxides are thermally more stable but decompose at ca. 100 °C.[13] The trisulfane-1-oxide **2** reported in this work is one of the most stable—if not the most stable—compounds of this type reported so far.

Experimental Section

The reactions were performed under an atmosphere of nitrogen. Solvents were dried and distilled before use.

To prepare **2**, ferrocene trisulfane **1** (0.714 mmol) in dichloromethane (50 mL) was oxidized by mCPBA (1.428 mmol) in dichloromethane (25 mL), which was added within 1 h. After stirring for an additional 15 min the mixture was washed several times with aqueous sodium hydrogencarbonate. The

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[9] For the properties of SS bonds at various coordination numbers see: Steudel, R. *Angew. Chem.* **1975**, *87*, 683, *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 655.

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[12] (a) Steudel, R.; Latte, J. *Chem. Ber.* **1977**, *110*, 423. (b) Derbesy, G.; Harpp, D. N. *J. Org. Chem.* **1995**, *60*, 4468. (c) Derbesy, G.; Harpp, D. N. *J. Org. Chem.* **1996**, *61*, 991. (d) Clennan, E. L.; Stensaas, K. L. *J. Org. Chem.* **1996**, *61*, 7911.

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organic phase was separated and dried over sodium sulfate. After filtration the solvent was removed under vacuum and the crude product purified by column chromatography on silica gel using first trichloromethane and then a mixture of trichloromethane and acetone (2:1) as an eluent. Red crystals of **2** (yield 74%) were obtained. Anal. Calcd for $C_{10}H_8FeOS_3$ (296.19): C, 40.55; H, 2.72; S, 32.47. Found: C, 40.36; H, 2.75; S, 31.82. MS (EI; *m*/*z*, ion, relative intensity(%)): 296, M^+ (90); 280, $[M^+ - O]$ (18); 248, $[M^+ - SO]$ (100); 184, $[(C_5H_4)_2Fe^+]$ (71); 152, $[(C_5H_4S)Fe^+]$ (36); 96, $[S_3^+]$ (27); 56, Fe^+ (32). ^1H NMR (200 MHz, CD_2Cl_2, 25 °C): δ 3.93 (m, 1H), 3.95 (m, 1H), 4.37 (pt, 2H), 4.49 (m, 1H), 4.54 (m, 1H), 4.69 (m, 1H), 4.80 (m, 1H). ^{13}C NMR (200 MHz, CD_2Cl_2, 25 °C): δ 66.9, 67.6, 70.2, 71.2, 72.2, 72.3, 72.4, 79.7, 90.3, 102.8.

When **2** (0.337 mmol), aminoiminomethane sulfinic acid[14] (0.656 mmol), and traces of iodine (0.024 mmol) were refluxed in acetonitrile (15 mL) for 4 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 (15 mL). The organic phase was first washed with aqueous sodium thiosulfate followed by water and dried over sodium sulfate. After evaporation of the solvent **1** was isolated in 94% yield (orange crystals, identified by CHS analysis, mp, IR, MS, Raman, and ^1H NMR spectra as compared to an authentic sample).

To prepare **3** from **1** (0.357 mmol) and mCPBA (1.07 mmol) the same procedure as for the preparation of **2** is applied. Yield: 32% after column chromatography with trichloromethane as an eluent. If **2** (0.506 mmol) is used as a starting material, somewhat less mCPBA (1.01 mmol) is needed. Yield: 60%. Anal. Calcd for $C_{10}H_8FeO_2S_3$ (312.19): C, 38.47; H, 2.58; S, 30.81. Found: C, 38.97; H, 2.54; S, 30.90. MS (EI; *m*/*z*, ion, relative intensity(%)): 312, M^+ (100); 248, $[(C_5H_4S)_2Fe^+]$ (62); 184, $[(C_5H_4)_2Fe^+]$ (8); 152, $[(C_5H_4S)Fe^+]$ (26); 56, Fe^+ (12). ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ 4.15 (s br, 1H), 4.49 (s br, 2H), 4.55 (s br, 1H), 4.91 (s br, 1H), 4.96 (s br, 1H), 5.31 (s br, 2H).

X-ray Crystallography. Crystal data are summarized in Table 1. The X-ray intensity data for **2** and **3** were collected on a Siemens SMART CCD area detector system equipped with a molybdenum target X-ray tube operated at 2.0 kW (50 kV, 40 mA). A total of 1246 frames of data (hemisphere) were collected with scan widths of 0.3° in ω and exposure times of 10 s/frame using a detector-to-crystal distance of 3.0 cm (maximum 2θ angle 61.2°). Frames were integrated to a maximum 2θ of 55.0° with the Siemens SAINT program.[15] Final unit cell parameters were determined from the least-squares refinement of 2701 reflections for **2** and 5402 for **3**. Data were corrected for absorption with the program SADABS[16] for **2**; no absorption correction was performed for **3**. The space groups were assigned as $P\bar{1}$ for **2** and $P2_1/n$ for **3**. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL.[17]

Table 1. Crystal Data, Data Collection, and Structure Refinement for 2 and 3

formula	$C_{10}H_8FeOS_3$	$C_{10}H_8FeO_2S_3$
fw	296.19	312.19
color	red	red
cryst size, mm	0.38 × 0.16 × 0.1	0.12 × 0.38 × 0.42
cryst system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
temp, K	293(2)	293(2)
wavelength, Å	0.71073	0.71073
a, Å	7.7175(2)	9.33880(10)
b, Å	7.8289(2)	9.8378(2)
c, Å	10.1986(2)	12.00280(10)
α, deg	81.5030(10)	90
β, deg	74.8840(10)	94.8330(10)
γ, deg	61.40	90
V, $Å^3$	522.09(2)	1098.82(3)
Z	2	4
density (calcd), g cm^{-1}	1.884	1.887
abs coeff, mm^{-1}	2.007	1.919
F(000)	300	632
scan range, deg	$3.14 \leq \theta \leq 27.50$	$27.49 \leq \theta \leq 99.4$
no. of reflns collected	3915	7911
no. of ind reflns	2323 ($R_{int} = 0.0610$)	2512 ($R_{int} = 0.0832$)
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/ params	2323/0/145	2512/0/145
goodness-of-fit on F^2	0.810	1.078
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0493, wR2 = 0.1240	R1 = 0.0375, wR2 = 0.0912
R indices (all data)	R1 = 0.0775, wR2 = 0.1393	R1 = 0.0487, wR2 = 0.0987
largest diff peak and hole, e $Å^{-3}$	0.603, −1.009	0.781, −0.558

In **2** the oxygen atom is disordered. In the difference map appeared two maxima possibly representing two oxygen atoms at sulfur atoms S1 and S3. When refined with occupation parameters of 1.0, the isotropic thermal parameters U_{iso} for both atoms showed high values of 0.11 and 0.14, respectively, and the R1 value was 0.0529. With site occupation factors *S* of 0.5, however, the U_{iso} parameters converged to reasonable values of 0.05 and 0.06, respectively, and an R1 value of 0.0458 was obtained. Refinement of the site occupation factors converged at $S = 0.63$ and 0.52, respectively. If normalized for one oxygen, $S = 0.55$ and 0.45. Therefore, a statistical 1:1 disorder was assumed. Anisotropic refinement with fixed occupation factors of 0.5 for both oxygen sites converged at 0.0430. For **3** two oxygen atoms at one sulfur atom were located. Both were refined with site occupation factors of 1.0; the resulting temperature factors did not show any anomalies.

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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 ORTEP drawings of **2** and **3**. This material is available free of charge via the Internet at http://publ.acs.org.

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[17] Sheldrick, G. M. *SHELXTL Software Reference Manual*, Version 5.1; Bruker AXS Inc.: Madison, WI, 1997.