

X-Ray Crystal Structure of 7,16,24,33-Tetrathia[3]paracyclo[3](1,3)-ferroceno[3]paracyclo[3](1,3)ferrocenophane¹⁾

Masao HISATOME,* Masamichi YOSHIHASHI, Koji YAMAKAWA, and Yoichi IITAKA†

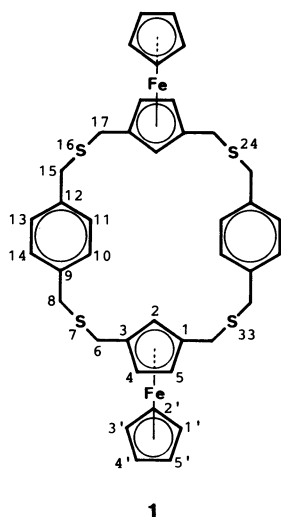
Faculty of Pharmaceutical Sciences, Science University of Tokyo,
12 Ichigaya-Funagawara, Shinjuku-ku, Tokyo 162

†Faculty of Pharmaceutical Sciences, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113

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Synopsis. The crystal structure of the title compound, a macrocyclic thioether containing two 1,3-ferrocene and two 1,4-benzene moieties, has been determined by X-ray diffraction. The compound is in a chair-like conformation in the crystal and solvated with one molecule of benzene which was used for crystallization.

Czech and Ratajczak²⁾ reported on the synthesis of ferrocene polythioethers by coupling reaction of 1,1'-bis(hydroxyalkyl)ferrocenes and alkanedithiols with trifluoroacetic acid (TFA) in dichloromethane. We applied the reaction to the synthesis of dithia[3]-benzeno[3]ferrocenophanes, which were used as synthetic intermediates of [2]benzeno[2]ferrocenophanes.^{3,4)} In these reactions of 1,3-bis(hydroxymethyl)ferrocene with TFA, an oligomeric compound **1** was the main product in coupling with 1,4-bis(mercaptomethyl)benzene, whereas reaction with 1,3-bis(mercaptomethyl)benzene gave mononuclear coupling product, 7,14-dithia[3]metacyclo[3](1,3)ferrocenophane (**3**),^{5,6)} in a good yield. The yield of **1** was always higher than that of mononuclear coupling product, 7,14-dithia[3]paracyclo[3](1,3)ferrocenophane (**2**), even though in high dilution conditions (10^{-3} mol dm⁻³).



The molecular structure of **1** could not unequivocally confirmed by spectroscopy. The mass spectrum by means of electron impact ionization showed the same spectral pattern as that of **2**. The peak corresponding to the molecular weight of binuclear coupling product (m/z 760) was detected by field desorption (FD) ionizing technique. Furthermore, treatment of **1** or **2** with TFA in dichloromethane gave

an equilibrium mixture of **1** and **2** (formation ratio, 3:1). These facts suggest that formation of **1** and **2** is thermodynamically controlled. Accordingly, it was not certain whether the peak observed in the FD mass spectrum indicates the exact molecular weight of **1**. On the other hand, there is no paper on the X-ray crystal structure of macrocyclic thioether containing metallocenes except for 1,1'-substituted metallocenes.^{7,8)} Therefore, determination of the crystal structure of **1** was carried out by X-ray diffraction.

Experimental

Material: Coupling reaction of 1,3-bis(hydroxymethyl)ferrocene and 1,4-di(mercaptomethyl)ferrocene with trifluoroacetic acid gave **1** (67%) and **2** (21%). The reaction conditions and the procedure were previously described.⁴⁾

Table 1. Atomic Coordinates ($\times 10^5$ for Fe; $\times 10^4$ for C and S) and Isotropic Equivalent Thermal Parameters (in Å² Unit) of **1** with Estimated Standard Deviations in Parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
Fe	18358 (10)	25292 (8)	54649 (8)	3.93
C(1)	1372 (7)	3071 (6)	3636 (6)	4.37
C(2)	1838 (7)	1967 (6)	3483 (5)	4.32
C(3)	3347 (7)	2191 (5)	4249 (6)	4.09
C(4)	3834 (7)	3419 (6)	4888 (6)	4.76
C(5)	2618 (7)	3974 (6)	4508 (7)	5.08
C(6)	4222 (8)	1250 (6)	4428 (6)	5.19
S(7)	5882 (2)	1432 (2)	3560 (2)	5.38
C(8)	5043 (8)	1302 (6)	1800 (6)	5.46
C(9)	3757 (7)	174 (6)	1254 (6)	4.50
C(10)	2574 (8)	274 (6)	253 (6)	5.29
C(11)	1352 (8)	-713 (6)	-272 (7)	5.46
C(12)	1227 (7)	-1827 (6)	164 (6)	4.77
C(13)	2430 (8)	-1940 (6)	1134 (6)	4.81
C(14)	3690 (8)	-949 (6)	1663 (6)	5.02
C(15)	-180 (8)	-2862 (7)	-338 (7)	5.66
S(16)	93 (2)	-4018 (2)	-1575 (2)	5.28
C(17)	162 (7)	-3253 (6)	-3064 (6)	5.10
C(1')	-32 (9)	2538 (8)	6388 (7)	6.59
C(2')	110 (9)	1352 (7)	6139 (7)	6.55
C(3')	1593 (9)	1314 (7)	6819 (7)	6.24
C(4')	2340 (9)	2526 (7)	7506 (6)	6.58
C(5')	1344 (10)	3260 (7)	7227 (7)	6.59
C(S1)	5451 (10)	5508 (7)	-1110 (9)	7.61
C(S2)	4197 (9)	5731 (7)	-614 (10)	7.93
C(S3)	3749 (9)	5224 (7)	491 (10)	7.66

Crystals of **1** were grown in a benzene-ethyl acetate solution as orange yellow plates of irregular shape.

X-Ray Crystallography: A crystal of approximate dimensions 0.1×0.2×0.3 mm was chosen for X-ray diffraction work. The cell dimensions and intensity data were collected on a Philips PW 1100 diffractometer using Mo K α radiation monochromated by a graphite plate. A total of 2588 reflections out of 3560 theoretically possible ones were measured as above the 2 $\sigma(I)$ level in a 2 θ range of 6–50°. Intensities were corrected for Lorentz and polarization factors but not for absorption.

(Crystal Data): 7,16,24,33-Tetrathia[3]paracyclo[3](1,3)ferroceno[3]paracyclo[3](1,3)ferrocenophane (**1**) benzene solvate; C₄₀H₄₀S₄Fe₂·C₆H₆; FW=838.8; triclinic; space group *P* $\bar{1}$; *a*=9.123(5), *b*=11.598(6), *c*=10.109(5) Å, α =96.10(5), β =97.95(5), γ =104.42(5)°; *U*=1014.9 Å³; *D*_{calc}=1.372 g cm⁻³; *Z*=1.

The molecule possesses a center of symmetry which lies on a crystallographic symmetry center. The presence of one molecule of benzene in a unit cell laying on another symmetry center was noticed during the refinement. The structure was solved by the heavy atom method and refined by the method of block-diagonal least-squares. The present *R* factor is 0.06 for 2588 reflections including anisotropic temperature factors for all atoms but hydrogen atoms are not included.

The atomic coordinates are listed in Table 1.⁹

Results and Discussion

The perspective ORTEP drawings are shown in Fig. 1. The compound **1** is a macrocyclic thioether

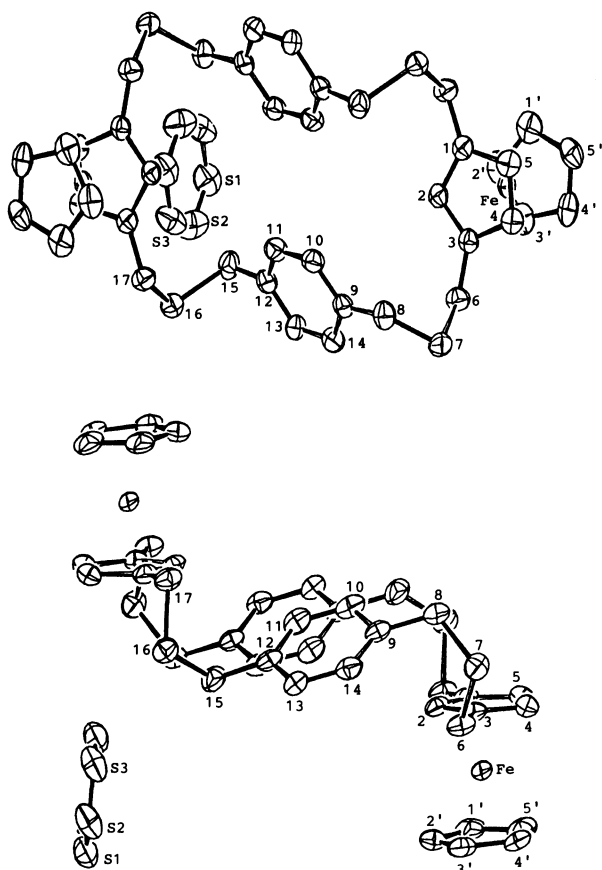


Fig. 1. ORTEP drawings (30% probability thermal ellipsoids) of **1**.

containing two ferrocene and two benzene moieties, as expected by FD mass spectrometry. The thioether **1** is the first example of macrocyclic 1,3-substituted ferrocenophane of which the structure was established by X-ray crystal analysis.

All bond lengths and angles⁹ are in almost normal ranges; the C–C distances of the cyclopentadienyl (Cp) rings, 1.413(12)–1.452(10) Å; the C–C distances of the benzene ring, 1.381(9)–1.410(9) Å; the C–S bond lengths, 1.812(7)–1.832(8) Å. The average distance of the substituted Cp ring carbons from the iron (2.046 Å) is almost similar to that of the unsubstituted ring carbons (2.054 Å). These results indicate that the macrocyclic ring is strain-free. On the other hand, inspection of mononuclear coupling product **2** with a Dreiding molecular model reveals its strained molecular structure, because the distance between the benzene and Cp ring planes in the most stable conformation is 2.5–2.7 Å, which would be enough space to cause mutual repulsion between the two rings. Therefore, the macrocyclic compound **1** is more thermodynamically stable than **2**. The experimental result that the macrocyclic compound **1** was formed in preference to [3.3]phane **2** in the synthetic reaction and under an equilibrium condition with TFA, as mentioned above, can be reasonably explained on the basis of the stabilities of their structures.

The conformation of **1** is in an interesting chair-like shape as a whole. The size of the macrocyclic cavity is about 3×6 Å. The planes of the two benzene rings of the phane are faced each other with a little inclination. The two ferrocene nucleus take an “anti” direction parallel to one another about the Cp–Fe–Cp axes. The rotational conformation about the Cp–Fe–Cp axis of each ferrocene moiety is almost eclipsed.

One molecule of benzene is packed in a unit cell as a solvent of crystallization. Attempted preparations of single crystals with other some solvents were unsuccessful. Accordingly, the benzene molecule would play an important role to the packing of the macrocyclic ring in crystallization.

References

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9) The anisotropic thermal parameters, the bond lengths

and angles, and the structure factors are deposited at the office of the Chemical Society of Japan (Document No. 8754).
