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PREPARATION AND SOME PROPERTIES OF POLYTHIA[n]FERROCENOPHANES

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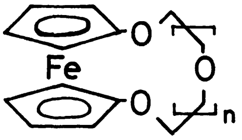
Polythiaferrocenophanes, **5**, and **8-12**, were prepared from 1,1'-ferrocenedithiol. Of these compounds, 1,4,7-trithia[7]ferrocenophane **8** showed an abnormal bathochromic shift in the electronic spectrum, and a downfield shift of the bridge-head carbons and an upfield shift of the other cyclopentadienyl carbons in the ^{13}C-NMR spectrum. Compounds **9-12** also showed complexing affinity to silver ion according to the size of polythia-macrocycles.

Much attention was focussed on the chemistry of the modified crown ether in order to develop a new functional ability. Incorporation of some hetero-atoms into the framework of a crown ether ring increases the affinity toward a transition metal ion.[1,2] Polyoxaferrocenophanes (**1**)[3,4] and (**2**),[5] which have an iron atom (a soft atom) of ferrocene nucleus in the crown ether ring, showed a weak complexing ability to an alkali metal cation (a hard atom), and a higher complexing ablity to silver and thallium cations (soft atoms). Oxathiaferrocenophanes (**3**) similarly made a stable complex with silver cation.[5] We now wish to report the preparation of polythia[n]ferrocenophanes, their increasing complexing ability with silver ion along with the increase in ring size, and a novel stereoelectronic phenomenon in 1,7-dithia[7]ferrocenophane.



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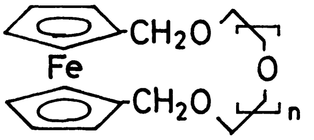

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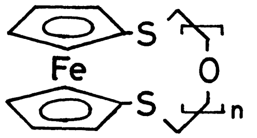
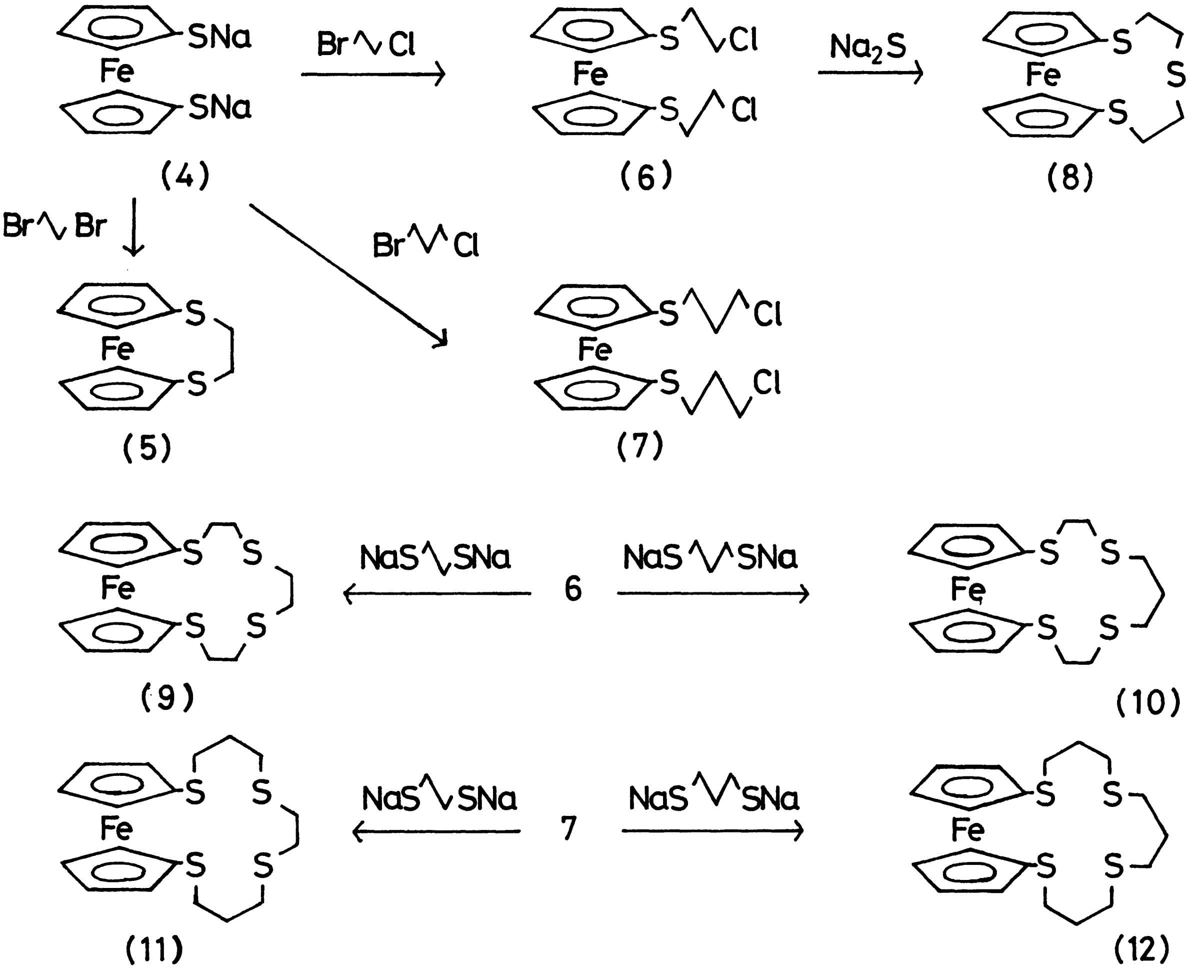


(3)

Disodium ferrocene-1,1'-dithiolate (**4**), which was prepared from the reaction of ferrocene-1,1'-dithiol[6] with aqueous sodium hyroxide in ethanol, was allowed to react with 1,2-dibromoethane in ethanol at room temperature to give 1,4-dithia-[4]ferrocenophane (**5**) as orange crystals in 37% yield. Similarly, **4** reacted with 1-bromo-2-chloroethane and 1-bromo-3-chloropropane to give 1,1'-bis(2-chloroethylthio)ferrocene (**6**) and 1,1'-bis(3-chloropropylthio)ferrocene (**7**) in 67 and 71% yields, respectively.



A solution of **6** in dry tetrahydrofuran was added all at once to a solution of sodium sulfide in anhydrous ethanol and the resulting solution was refluxed for 10 h. After an usual work-up, the reaction product was purified by column chromatography on silica gel to give 1,4,7-trithia[7]ferrocenophane (**8**) as orange leaflets in 27.5 % yield. Similarly, **6** reacted with disodium ethanedithiolate and propanedithiolate under relfuxing for 5 h to give 1,4,7,10-tetrathia[10]- (**9**) and 1,4,8,11-tetrathia[11]ferrocenophane (**10**) in 31 and 59.1% yields, respectively. Compound (**7**) also reacted with disodium ethanedithiolate and propanedithiolate to give 1,5,8,12-tetrathia[12]- (**11**) and 1,5,9,13-tetrathia[13]ferrocenophane (**12**) in 35 and 64% yields, respectively. The structure of these new compounds was determined by the elemental analysis and spectral data summarized in Tables 1 and 2. In the ^{1}H-NMR spectrum of **5**, the proton signals of ferrocene ring appeared as two triplets at δ 4.40 and 4.17, but those of other **9** - **12** appeared as a sharp singlet. The remarkable splitting of α- and β-protons of ferrocene ring in **5** may be probably due to the ring-tilt deformation of ferrocene nucleus by the dithioethylene chain which combines the two cyclopentadienyl rings.[7] As shown in Table 1, 1,4,7-trithia[7]ferrocenophane **8** showed an abnormal bathochromic shift ($\Delta\lambda$ 20 nm) and the increase of the absorbance ($\Delta\varepsilon$ ca. 40) of the absorption band near 440

Table 1. Yield, M.p., and Electronic Spectrum of Polythiaferrocenophanes

Compd.	**5**	**8**	**9**	**10**	**11**	**12**
Yields(%)	37	28	31	59	35	64
M.p.(°C)	138-9	120	116	75	98	60
λ_{max}(nm)	438	461	442	443	443	443
ε	138	272	223	196	191	190

Table 2. ^{1}H-NMR and ^{13}C-NMR Spectra of Polythiaferrocenophanes

Compd.	^{1}H-NMR(90 MHz)(δ , Hz)	^{13}C-NMR(22.5 MHz)(δ)
5	4.38(t, 4H, J=1.9), 4.16(t, 4H, J=1.9) 3.28(s, 4H)	85.0(C_b), 70.0(C_α), 68.7(C_β), 31.1(SCH_2)
8	4.29(t, 4H, J=1.8), 4.21(t, 4H, J=1.8), 2.9-3.5(m, 8H)	89.7(C_b), 70.6(C_α), 67.5(C_β), 37.2, 32.8(SCH_2)
9	4.21(m, 8H),3.07(s,4H), 3.0-3.3 and 2.7-3.0(A_2B_2 pattern, 4H)	85.3(C_b), 72.1(C_α), 68.9(C_β), 38.3. 32.6. 31.1(SCH_2)
10	4.21(s, 8H), 3.0-3.2(m, 4H), 3.0-3.7 (m, 8H), 2.02(p, 2H, J=6.1)	85.3(C_b), 72.0(C_α), 68.8(C_β), 36.8, 31.9, 31.3, 30.4(SCH_2)
11	4.21(s, 8H), 2.84(s, 4H), 2.7-3.0 (m,8H), 1.91(p, 4H, J=6.1)	84.3(C_b), 72.9(C_α), 68.9(C_β), 34.9, 32.1, 30.0, 29.1(SCH_2)
12	4.20(s, 8H), 2.5-3.0(m, 12H), 1.7-2.2(m, 6H)	84.1(C_b), 72.9(C_α), 68.9(C_β) 35.0, 30.8, 30.2, 28.9(SCH_2)

nm characteristic of ferrocene, which is assigned to d-d transition from the HOMO to the LUMO.[8] In the ^{13}C-NMR spectrum of **8**, the signal of the bridge-head carbon shifted downfield ($\Delta\delta$ ca. 4 ppm) and the signals of α- and β-carbons of cyclpentadienyl rings of ferrocene nucleus shifted upfield ($\Delta\delta$ 0.6-2.3 ppm). A similar trend was also observed in 4-oxa-1,7-dithia[7]ferrocenophane.[5] There is no strain causing the tilt-deformation of two cyclopentadienyl rings in this molecule on considering the HGS molecular model of **8**. The abnormal shifts observed in the electronic and ^{13}C-NMR spectra may be then interpreted by an interaction either between ferrocene nucleus and sulfur atom in the 4-position or between ferrocene nucleus and the sulfur atom in the 1- and 7-positions of **8**. The former possibility will be excluded by the fact that such an abnormal shift was not observed in 1,4,7-trioxa[7]ferrocenophane[3] and 1,7-dioxa-4-thia[7]ferrocenophane.[9] From consideration of the stereo-model of **8**, the hybrid orbital of the lone pair of sulfur atom is arranged to be perpendicular to the plane of cyclopentadienyl ring. Therefore, of some possible interactions, two interactions may likely remain to interpret the spectroscopic characteristics observed in **8** and the related compounds. First, an interaction between the non-bonding d-orbital on the iron atom and the lone-pair of sulfur atom seems to contribute to the bathochromic shift of **8**. The interaction between the lone pair of sulfur atom and the Fe-C bond connecting the cyclopentadienyl ring to the iron atom (σ-π conjugation)[10] may also explain the abnormal chemical shift of carbon atom described above. Both interactions may also cause these spectral phenomena in **8**.

Table 3. Electronic Spectral Hypsochromic Shift and Absorbance Decrease on Addition of $AgNO_3$ in CH_3CN

Compd.	$\Delta\lambda_{max}$(nm)	$\Delta\varepsilon$	Compd.	$\Delta\lambda_{max}$(nm)	$\Delta\varepsilon$
9	6	9	**3b**(n=2)	10	10.1
10	13	13	**3b**(n=3)	15	18.3
11	11	25	**3c**(n=4)	14	13.1
12	17	17			

On addition of silver nitrate to **9** - **12** in acetonitrile, the absorption band near 440 nm showed a hypsochromic shift and a decrease of its absorbance, as shown in Table 2. It seems to exist a parallel relationship between the magnitude of the hypsochromic shift and the decrease of absorbance. The increasing hypsochromic shift corresponding with the increasing size of polythia-macrocycles may be explained by the fitness of silver cation to the polythiaferrocenophanes. As shown in Table 3, a similar relationship was observed in oxathiaferrocenophane series.[5] The isolation and physicochemical study of the complex of the polythiaferrocenophanes with silver and other metal salts are in progress.

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