Tetrahedron Letters,Vol.23,No.2,pp 185-188,1982 0040-4039/82/020185-04$03.00/0
Printed in Great Britain

PREPARATION AND SOME PROPERTIES OF POLYOXATHIAFERROCENOPHANES

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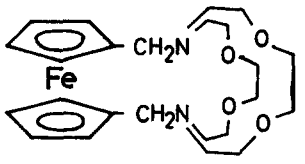
Summary: Some sulfur analogs of a crown ether-like compound containing ferrocene as a ring member were prepared. Their complexing ability was poor with alkali metal cations but good with a silver cation.

A great number of macrocyclic compounds containing oxygen, nitrogen, and sulfur are used as a phase-transfer catalyst and a selective ion-transfer.[1] Polyoxathiaferrocenophane is a crown ether-like compound including ferrocene as a ring member, in which the iron atom may play a role of co-ordinatable heteroatom. In regard to ferrocenophanes, therefore, it is of interest how the cation-complexing ability will be influenced by the intervening iron atom, and what kind of interaction will be expected between the iron atom and the complexed cation. This class of compounds, for example, 1 and 2, were prepared by three groups,[2-4] but they seem to have too long distance between the iron atom and the center of the macrocycle to interact on each other. Polish workers recently reported the preparation of polyoxaferrocenophanes (3), and supposed by the UV spectra that there was no such interaction.[5] We now report the preparation and some properties of the sulfur analogs of polyoxaferrocenophanes, 4 and 5.



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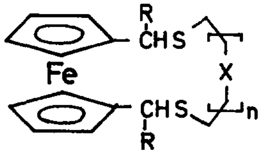

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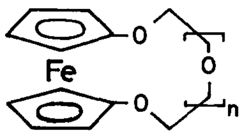

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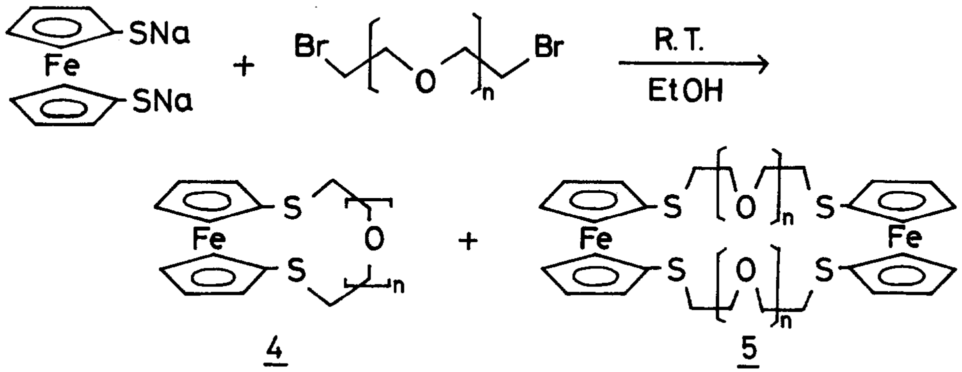
Disodium ferrocene-1,1'-dithiolate was allowed to react with 1,11-dibromo-3,6,9-trioxaundecane in ethanol at room temperature to give a mixture of mononuclear 4,7,10-trioxa-1,13-dithia[13]ferrocenophane (4c)(64%) and binuclear 4,7,10,27,30,33-hexaoxa-1,13,24,36-tetrathia[13,13]ferrocenophane (5c)(17%). The cyclopentadienyl ring protons in the PMR spectrum of 4c appeared as a



a: n=1 b: n=2 c: n=3 d: n=4

multiplet centered at δ 4.25, while those of 5c appeared as a pair of triplets at δ 4.34 and 4.23. In both cases the methylene protons between sulfur and oxygen atoms appeared in A_2X_2 type, that is, two well-separated triplets at δ 3.03 and 3.74 for 4c and at δ 2.81 and 3.62 for 5c. The other methylene protons appeared as singlets at δ 3.71 for 4c and δ 3.61 for 5c. In mass spectra, 4c and 5c showed the molecular ion peaks at m/e 408 and 816, respectively. These spectral data assure the assignment of their structures.

Disodium ferrocene-1,1'-dithiolate reacted similarly with 1,8-dibromo-3,6-dioxaoctane to afford 4,7-dioxa-1,10-dithia[10]ferrocenophane (4b)(26%) and 4,7,24,27-tetraoxa-1,10,21,30-tetrathia[10,10]ferrocenophane (5b)(12%). A similar reaction of the dithiolate with 1,14-dibromo-3,6,9,12-tetraoxatetradecane, however, gave only mononuclear 4,7,10,13-tetraoxa-1,16-dithia[16]ferrocenophane (4d) in 60% yield. The reaction of the dithiolate with 1,5-dibromo-3-oxapentane was somewhat complex, but from the reaction mixture 4-oxa-1,7-dithia[7]ferrocenophane (4a)(8%) and 4,21-dioxa-1,7,18,24-tetrathia[7,7]ferrocenophane (5a)(30%) were isolated. The reaction of the dithiolate with 1,5-dichloro-3-oxapentane in refluxing butanol gave a similar result. The increasing yield of the ferrocenophane 4 according as the increasing number of member in the polyoxathiaether chain may be due to a template effect by the cation.[6] A PMR spectral comparison of mononuclear products 4 with binuclear ones 5 is particularly interesting (Table 1). The ferrocene ring protons in 4 appeared as a narrow multiplet or a singlet, while those in 5 appeared as two close triplets. The methylene protons next to sulfur in 4 appeared at low magnetic field by 0.3 ppm than the corresponding protons in 5. A similar trend was also observed in the methylene protons next to oxygen atom. Such differences may be explained by using the deshielding-shielding model of a ferrocene nucleus proposed by Mulay and Fox.[7] Both of the methylene protons next to sulfur and oxygen atoms in 4 are forced to be immersed in the deshielding zone, but those of 5 are out of its influence.

It was shown that polyoxaferrocenophanes have a strong complexing ability with an alkali metal cation.[5] This indicates that the incorporation of the iron

Table 1. M.p. and Spectral Data of Polyoxathiaferrocenophanes

Compound	m.p.(°C)	MS	PMR(δ , Hz)
4a	62-63	320 (M^+, 100%)	3.07 (t, 4H, J=5.5), 3.94 (t, 4H, J=5.5), 4.20 (m, 8H)
5a	112-113	640 (M^+,100%) 320 (32%) 304 (30%)	2.88 (t, 8H, J=5.8), 3.64 (t, 8H, J=5.8), 4.25 (t, 8H, J=1.7), 4.41 (t, 8H, J=1.7)
4b	oil	364 (M^+, 100%)	3.06 (t, 4H, J=6.2), 3.75 (s, 4H) 3.86 (t, 4H, J=6.2), 4.24 (s, 8H)
5b	oil	728 (M^+, 100%) 364 (56%), 304 (25%)	2.67 (t, 8H, J=6.2), 3.59 (s, 8H) 3.64 (t, 8H, J=6.2), 4.24 (t, 8H, J=1.7), 4.35(t, 8H, J=1.7)
4c	oil	408 (M^+, 100%)	3.03 (t, 4H, J=6.0), 3.71 (s, 8H) 3.74 (t, 4H, J=6.0), 4.25 (s, 8H)
5c	84-85	816 (M^+, 100%) 408 (42%)	2.81 (t, 8H, J=6.5), 3.61 (s, 16H) 3.62 (t, 8H, J=6.5), 4.23 (t, 8H, J=1.7), 4.34 (t, 8H, J=1.7)
4d	oil	452 (M^+, 100%)	2.95 (t, 4H, J=6.0), 3.69 (s, 12H) 3.69 (t, 4H, J=6.0), 4.24 (m, 8H)

atom of ferrocene nucleus (a soft atom) into crown ether chain has little influence on the complexing ability with an alkali metal cation (hard acid). On the basis of HSAB principles[8] it will be anticipated that the displacement of some oxygen atoms by sulfur atoms on polyoxaferrocenophane decreases the affinity to a hard cation and increases the affinity to a soft heavy metal cation. A complexing ability of polyoxathiaferrocenophanes prepared here with an alkali metal cation was examined by the extraction method described by Pedersen.[9] Compound 4d showed a little complexing ability (0.6%) and 4a-c did no complexing ability with sodium and potassium cations. The complexation of 4 and 5 with a silver cation, on the other hand, took place excellently. The extraction data were summarized in Table 2. Except for 4a which was oxidized with $AgNO_3$ and 4b in which the size of hetero-crown ether ring is not enough to complex with a silver ion, the polyoxathiaferrocenophanes 4 and 5 showed a high complexing ability with a silver ion. The trend observed in the pressnt work is comparable with that in benzooxathiacyclopolyethers.[10]

On the addition of $AgNO_3$ to 4 and 5 in acetonitrile, the absorption band near 440 nm, characteristic of ferrocene nucleus, showed a hypsochromic shift and decrease of its absorbance. The results were summarized in Table 2. There seems to be a parallel relationship between the hypsochromic shift and the decrease of absorbance in the mononuclear series 4b-d, but no in the binuclear series 5a-c. Both of the extraction ability and the change of UV spectrum were small in 4b and

Table 2. Extraction Ability and Change of UV Spectra

Compound	Extraction ability of silver ion (%)	Change of UV spectra on addition of $AgNO_3$ Hypsochromic shift (nm)	Decrease of absorbance (%)
4b	49.1	10	10.1
4c	77.3	15	18.3
4d	78.9	14	13.2
5a	77.1	11	9.1
5b	84.7	3	10.7
5c	93.5	7	11.6

large in 4c and 4d, suggesting that there is a certain relationship between the extraction ability and the change of UV spectrum in this series of compounds. The extraction ability of 4c was almost similar with that of 4d, but the change of UV spectrum of 4c was larger than that of 4d. The fact suggests that a silver ion can complex more strongly with 4c than 4d. Such a large change of UV spectrum which depends on the complexing ability of those crown ether compounds should be worthy of notice. In the PMR spectrum (CD_3CN) of 4d, the addition of $AgNO_3$ (one equivalent and over) causes a deshielding shift by 0.08 ppm of the signal of methylene protons next to sulfur atom and a desielding shift by 0.21 ppm of the ring proton signal of the ferrocene nucleus. The shape of the latter signal (singlet) remained unchanged. The similar change was also observed in 4c. These facts seem to suggest a certain interaction between the iron atom of ferrocene nucleus and the complexed silver ion. The work investigating such an interaction is now in progress.

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(Received in Japan 10 August 1981)