  Bull. Chem. Soc. Jpn., 57, 421—425 (1984)

Preparation and Spectral Behavior of Polyoxadithia[*n*]ferrocenophanes and Their Silver(I) Nitrate Complexes

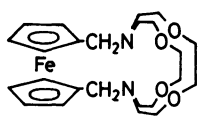
Masaru SATO, Masao KUBO, Seiji EBINE,*,† and Sadatoshi AKABORI††
Chemical Analysis Center, Saitama University, Urawa, Saitama 338
†*Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama 338*
††*Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba 274*
(Received May 20, 1983)

Polyoxadithia[*n*]ferrocenophanes and polyoxatetrathia[*n.n*]ferrocenophanes were prepared by treatment of 1,1′-ferrocenedithiol with α,ω-dibromo polyethers. The ferrocenophanes formed efficiently a complex with a silver ion, but not with alkali and alkali-earth metal ions. The spectral data of the silver ion-complexed ferrocenophanes suggested the presence of a partial electron-transfer interaction between the iron atom and the complexed silver ion.

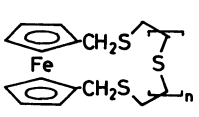
In order to develop a new functional ability, various attempts to prepare modified crown ethers have been made.[1] Incorporation of a certain heteroatom into a crown ether ring increases a complexing affinity with transition metals. For example, polythiamacrocycles are able to form a stable complex with silver(I),[2] nickel(II),[3] and copper(II) salts.[4] Polyoxathiaferrocenophane is a crown ether-like compound containing a ferrocene ring and a sulfur atom as ring members, in which the iron atom of the ferrocene may play a role of a coordinatable heteroatom to a complexed cation. A few were reported about this class of compounds. For example, 1,1′-ferrocenedicarbonyl dichloride reacted with a diazacrown ether and the product was reduced to give the ferrocene derivatives (**1**) of cryptand.[5] Polythia- (**2**)[6] and dithiaoxaferrocenophanes (**3**)[7] were prepared from 1,1′-ferrocenedimethanol and its derivatives. In these compounds, however, the distance between the iron atom of the ferrocene and the center of the macrocycle is too long to effect an interaction between the iron atom and the complexed metal ion. Polish workers[8] recently prepared polyoxaferrocenophanes (**4**) carrying oxygen atoms attached directly to a ferrocene nucleus, and suggested, from their electronic spectra, no interaction between the iron atom and the complexed rubidium cation. We also prepared polyoxaferrocenophanes and discussed their complexing ability and interaction between the iron atom and the complexed metal cations.[9] We now report the preparation and some complexing properties of polyoxadithiaferrocenophanes, carrying sulfur atoms attached to the ferrocene nucleus.[10]

Syntheses and Spectral Properties. Disodium 1,1′-ferrocenedithiolate, prepared from 1,1′-ferrocenedithiol[11] and aqueous sodium hydroxide in ethanol, reacted with α,ω-dibromo polyethers in ethanol at room temperature and the products were chromatographed by a silca-gel column to give two kinds of oxathiaferrocenophanes (**5**) and (**6**). The structures were determined by the elemental analyses and spectral data. For example, the molecular formula of **5c** was deduced to be $C_{18}H_{24}O_3S_2Fe$ by the elemental analysis and mass spectroscopy (M^+ 408). In the ^{1}H-NMR spectrum of **3d**, the α- and β-ring protons of the ferrocene nucleus appeared as a singlet (8H) at δ 4.24, while the methylene protons next to the oxygen atom appeared as a triplet (4H, J=6 Hz) at δ 3.74 and a singlet (8H) at 3.71, and those next to the sulfur atom resonated as a triplet (J=6.0 Hz) at δ 3.03. In the ^{13}C-NMR spectrum of **5c**, the bridgehead carbon (C_b), α- and β-carbons of the ferrocene nucleus resonated at δ 84.8, 72.7, and 68.8, respectively. In addition, the signal of the carbon next to the sulfur atom appeared at δ 35.8 and those next to the oxygen atoms appeared at δ 69.5, 70.5, and 70.7.

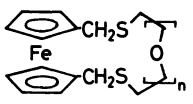
The yield of polyoxadithia[*n*]ferrocenophanes (**5**) amounted to maximum when n=3, but that of polyoxatetrathia[*n.n*]ferrocenophanes (**6**) decreased with the increase of the size of the macrocycle, which may indicate that a template effect of sodium cation plays a little role in the final cyclization step. As shown in the ^{1}H-NMR spectral data of Table 2, there is a remark-



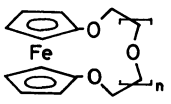
(1)



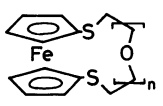
(2)



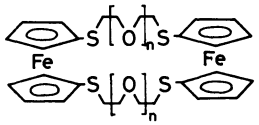
(3)



(4)

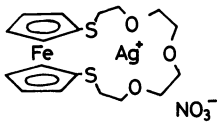


(5)



(6)

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



(7)

able difference in the pattern of ferrocene ring protones between mononuclear compounds **5** and dinuclear compounds **6**. In the former, the α- and β-ring protons of the ferrocene nucleus resonated as a singlet or a narrow multiplet, but in the latter the corresponding protons appeared as a pair of triplets. The methylene protons next to the sulfur atom in **5** resonated at lower field by 0.3 ppm than the corresponding ones in **6**. A similar trend was also observed in the methylene protons next to the oxygen atom. The low-field shift of the methylene protons in the mononuclear ferrocenophane **5** would be probably due to the fact that those protons exists in the deshielding zone of a ferrocene nucleus (an interannular area)[12] according to consideration of its stereomolecular model.

In the ^{1}H-NMR spectra of the ferrocene ring protons, **5a—d** have a similar chemical shift (δ *ca.* 4.2) to each other. In the ^{13}C-NMR spectra of the ferrocene ring carbons, however, **5a** showed a trend different from the other mononuclear ferrocenophanes **5b—d**, that is, the bridge-head carbon atom resonated at a lower field ($\Delta\delta$ *ca.* 6 ppm) and the α- and β-carbon atoms of **5a** resonated at a higher field ($\Delta\delta$ *ca.* 2 ppm) in **5a** than in the other **5b—d**. A similar specificity of **5a** was also observed in the electronic spectra of **5** (Table 1).

The absorption band near 440 nm of **5a**, assignable to a d-d transition of ferrocene nucleus,[13] shifted to a longer wavelength region ($\Delta\lambda$ *ca.* 10 nm) than that of **5b—d**, and its absorbance increased considerably (*ca.* 40%), the details of which will be discussed in another paper.[14]

Complexing Ability. The complexing ability of polyoxaferrocenophanes (**4**) with alkali metals was first reported to be conspicuous by the TLC method,[8] but was recently shown to be rather faint by the extraction method.[9] This trend is comparable with the fact that the complexing ability of benzocrown ether with alkali metal cations is smaller than that of crown ether itself, the reason of which has been rationalized by the HSAB principles.[15] On the basis of this principle, the displacement of some oxygen atoms of **4** by the sulfur atoms to **5** and **6** will results in a decrease in the affinity to hard cations and an increase in the affinity to soft heavy metal cations. The complexing ability of **5** and **6** with a variety of metals cation was examined by the extraction method described by Pedersen,[16] and the results were summarized in Table 3, alkali and alkali-earth metal cations being excluded because no extraction ability toward them was observed. This result is coincident with the expectation described above. The complexing ability of **5** and **6** was a little

Table 1. Electronic spectral data of **5** and **6**

Compd	**5a**	**5b**	**5c**	**5d**	**6a**	**6b**	**6c**
λ_{max}/nm	456	444	443	440	438	438	438
ε	242	198	198	192	351	363	379

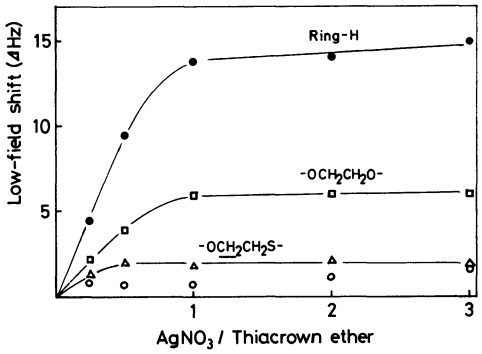


Fig. 1. ^{1}H-NMR spectral change of **5c** on addition of silver(I) nitrate in acetonitrile-d_3.

Table 2. ^{1}H-NMR and ^{13}C-NMR spectra of **5** and **6** ($CDCl_3$)

Compd	^{1}H-NMR (60 MHz)	^{13}C-NMR (22.5 MHz)
5a	4.20(m, 8H), 3.94(t, 4H, J=5.5), 3.07(t, 4H, J=5.5)	90.7(C_b), 66.9(C_α), 70.0(C_b), 34.7(SCH_2), 71.4(OCH_2)
5b	4.24(s, 8H), 3.86(t, 4H, J=6.2), 3.75(s, 8H), 3.06 t, 4H, J=6.2)	85.4(C_b), 68.3(C_α), 72.7(C_β), 35.6 (SCH_2), 69.6 and 71.0(OCH_2)
5c	4.25(s, 8H), 3.74(t, 4H, J=6.0), 3.71(s, 8H), 3.03(t, 4H, J=6.0)	84.8(C_b), 68.8(C_α), 72.7(C_β), 35.8 (SCH_2), 69.5, 70.5, 70.7(OCH_2)
5d	4.24(m, 8H), 3.69(t, 4H, J=6.0), 3.69(s, 12H), 2.75(t, 4H, J=6.0)	83.8(C_b), 69.3(C_α), 73.4(C_β), 36.5(SCH_2), 69.5, 70.5, 70.7(OCH_2)
6a	4.41(t, 8H, J=1.7), 4.25 (t, 8H, J=1.7), 3.64(t, 8H, J=5.8), 2.88(t, 8H, J=5.8)	
6b	4.35(t, 8H, J=1.7), 4.24 (t, 8H, J=1.7), 3.64(t, 8H, J=6.2), 3.59(s, 8H), 2.67(t, 8H, J=6.2)	
6c	4.34(t, 8H, J=1.7), 4.23 (t, 8H, J=1.7), 3.62(t, 8H, J=6.5), 3.61(s, 16H), 2.81 (t, 8H, J=6.5)	

Table 3. Extraction ability of **5** and **6**

Compd	Cd^{2+}	Pb^{2+}	Tl^+	Ag^+
5a	1.9	Nil	1.5	—
5b	2.9	Nil	1.5	49.1
5c	3.1	Nil	12.5	77.3
5d	3.3	19.2	43.9	78.9
6a	3.3	1.4	7.0	77.1
6b	2.9	1.0	20.0	84.7
6c	2.7	1.5	42.8	93.5

Table 4. Hypsochromic shift of electronic spectra in acetonitrile and low-field shift of ^{1}H-NMR spectra in acetonirile-d_3 of **5** in the presence of silver(I) nitrate (1 equiv)

Compd	Electronic spectra near 440 nm $\Delta\lambda_{max}$/nm	$\Delta\varepsilon$/%	^{1}H-NMR spectra Ring-H		(Δ, ppm) S-CH_2
5b	10	−10.1	0.32	0.20	0.15
5c	15	−18.3	0.17		0.01
5d	14	−13.1	0.21		0.08

or negligible with lithium, sodium, potassium, calcium, strontium, cadmium, and lead cations, while it was excellent with a silver cation and moderate with a thallium ion. The high complexing ability with a silver ion is comparable with that of benzooxathiacyclopolyethers.[2] It is also noteworthy that lead and thallium ions showed a remarkable dependence on the size of the macrocycle of **5** and **6**.

On addition of silver nitrate to **5** and **6** in acetonitrile, the absorption band near 440 nm showed a hypsochromic shift and a decrease in its absorbance, which are summarized in Table 4. There seems to be a parallel relationship between the hypsochromic shift and the decrease in absorbance in the mononuclear series **5b—d**, but not in the binuclear series **6a—c**. Both of the complexing ability and the electronic spectral change are large in **5c** and **5d**, but small in **5b**. This parallel relationship suggests an importance of the fitness of the macrocycles in **5** with a silver ion. The change of electronic spectra of a crown ether on addition of a metal cation is reported to be small.[17] So, a large electronic spectral change which depends on the complexing ability of those crown ether-type compounds presented here should be noticable.

In the ^{1}H-NMR spectrum of **5** in acetonitrile-d_3, the addition of silver nitrate causes a deshielding shift of the signals of methylene protons next to the sulfur atom and the ferrocene ring protons (Table 4). As shown in Fig. 2, the deshielding shift ($\Delta\delta$) increases almost linearly according to the increase of silver nitrate until the amount of the salt becomes equivalent to polyoxadithiaferrocenophanes **5**, but the addition of more silver ion results in little change of deshielding shift, which suggests the formation of a 1:1 complex of the ferrocenophanes 5 with silver nitrate in acetonitrile. The ferrocene ring protons of the complex of **5c** and **5d** with silver(I) nitrate appeared as a singlet just like those of free **5c** and **5d**, while the α- and β- protons of ferrocene ring protons of the complexed **5b** resonated as a separated pair of triplets. This is probably because the complex formation of **5b** with silver(I) nitrate demands the tilt-deformation of two cyclopentadienyl rings in order to put the silver(I) ion in the hole by spreading the macrocycle, because it is well known that the tilt-deformation of the cyclopentadienyl ring in ferrocenophanes causes the splitting of the α- and β-protons of ferrocene ring.[18] Since the tilting of two cyclopentadienyl rings results in some bathochromic shift,[18] the small change in the electronic spectrum of **5b** described above may reflect the difficulty on complexation of **5b** with a silver ion.

The deshielding of methylene protons on the complexation of **5** may be caused by the magnetic anisotropy of the silver ion. However, the large deshielding ($\Delta\delta$ *ca.* 0.2 ppm) of the ferrocene ring protons seems to be due to the electron density of the cyclopentadienyl rings decreased by a partial electron transfer from the iron atom to the complexed silver ion in **5**, since the α-and β-protons shifted to the same extent. If the deshielding shift is caused by the perturbation of the inductive and conjugative effect of the sulfur-substituent with coordination of a silver ion to a sulfur atom, the α-protons would be expected to resonate at a lower field than the β-protons. (The influence of an electron attracting substituent is well known to appear at the α-protons more remarkably.) Such a partial electron transfer has been observed in the complex of 1,1′-bis(diphenylphosphino)ferrocene with mercury(II) chloride.[19] An additional support was obtained from the ^{13}C-NMR spectra of **5b—d** and its benzene analog measured in the presence of silver(I) nitrate in acetonitrile-d_3 (Table 5).

Table 5. Low-field shift of ^{13}C-NMR spectra on additon of silver(I) nitrate to a solution of **5** in acetonitrile-d_3 (Δ, ppm)

Compd	C_b	C_α	C_β	SCH_2
5b	−3.2	1.1	2.0	1.3
5c	−8.2	4.2	2.8	3.9
5d	−6.4	3.5	2.2	3.2
8	−4.0	−1.5	1.5	2.7

a) C_b means the bridgehead carbon.

The signal of the α- and β-carbon of ferrocene ring in **5b—d** shifted down-field but those of the bridgehead carbon shifted up-field. The deshielding shift of methylene carbons next to a sulfur atom was similar to that of the ferrocene ring carbones, but the methylene carbons next to an oxygen atom showed only a little shift. In the benzene analog 4′-methyl-2,3-benzo-1,4-dithia-7,10,13-trioxa-2-cyclopentadecene (**8**),[2] on the other hand, the bridgehead carbon and methylene carbons next to sulfur atoms showed the same trend with in **5**, but the α-ring carbons showed some upfield shifts, suggesting a significant complexing of the silver ion with the sulfur atom. The fact that the ferrocene ring carbons (C_α and C_β) in **5** showed more deshielding shift than the corresponding benzene ring carbons in **8** suggest some electron transfer from the iron atom to the complexed silver ion on addition to the electron transfer *via* the sulfur atom from the cyclopentadienyl ring to the silver cation. Finally, the complexation of **5c**, among **5**, with silver(I) ion would be the strongest because the change of the carbon chemical shifts in the ^{13}C-NMR spectra was the largest in **5c**. The length of an oxyethylene chain in **5** would probably control the fitness of the macrocycle to a silver(I) ion.

Complex of 5c with Silver(I) Nitrate. A solution of **5c** and an equimolar silver(I) nitrate in acetonitrile was poured into anhydrous ether under nitrogen to give stable yellow crystalline precipitates of the 1:1 complex (7). However, **5b** and **5d** gave no crystalline complex. This result is coincident with suggestion described above that **5c** will form the most tight complex with silver(I) nitrate among **5**. The ^{1}H-NMR spectrum of **7** in $CDCl_3$ showed a pair of triplets corresponding to the H_α and H_β protons of a ferrocene nucleus at δ 4.50 and 4.33 (J=2.0 Hz), a pair of triplet assigned to the protons next to a sulfur atom and next to an oxygen atom at δ 3.04 and 3.74 (J=5.8 Hz) respectively, and a singlet at δ 3.77 ($-OCH_2CH_2-$). The difference in the chemical shift between free ligand **5c** and complex **7** is almost similar to that measured on

addition of silver(I) nitrate to a solution of **5c** in acetonitrile-d_6. The ferrocene ring protons appeared as a pair of triplet in the former but a broad singlet in the latter. This seems to be probably because in the latter, there is an equilibrium between the free ligand and the complex in acetonitrile and hence the signals of α- and β-protons are avaraged to an single signal. The fact that the splitting of the ferrocene ring protons was observed in the isolated silver-complex (**7**) indicates that the through-space electronic interaction between the iron atom of a ferrocene nucleus and the complexed silver ion in **7** described in the preceding section is too emphasized.

The ^{13}C-NMR spectrum of **7** in $CDCl_3$ showed the signals of bridge-head, α-, and β-carbons appeared at δ 77.7, 77.1, and 71.1 ppm, respectively. The carbons next to a sulfur atom appeared at δ 40.0 ppm, and those next to an oxygen atom appeared at δ 70.4, 69.7, and 67.2 ppm. The deshielding shifts of α- and β-carbons of ferrocene ring and the sulfur-attached carbons in **7** are almost similar to those measured on the addition of silver(I) nitrate to a solution of **5c** in acetonitrile-d_3. These NMR data of **7** indicate that **5c** and probably other polyoxadithiaferrocenophanes (**5b** and **5c**) also form a 1:1 complex in acetonitrile, and that the discussion about the nature of the complex of **5** with silver(I) nitrate described in the preceding and present section is reasonable enough.

Experimental

The melting points are uncorrected. The electronic spectra were measured on a Hitachi 340 Spectrometer. The IR spectra were measured on a JASCO IRA-2 Infrared Spectrometer. The ^{1}H-NMR and ^{13}C-NMR spectra were obtained on a JEOL FX-90Q Spectrometer, TMS being chosen as an internal standard. The mass spectra were taken by using a Hitachi M-80 Spectrometer.

Material. 1,1′-Ferrocenedithiol was prepared by reduction of 1,2,3-trithia[3]ferrocenophane with lithium aluminum hydride.[11] Bis(2-bromoethyl) ether,[20] 1,8-dibromo-3,6-dioxaoctane,[20] 1,11-dibromo-3,6,9-trioxaundecane,[21] and 1,14-dibromo-3,6,9,12-tetraoxatetradecane were prepared according to the literatures.

Polyoxadithia[n]*ferrocenophanes(5) and Polyoxatetrathia*-[n.n]*ferrocenophanes. General Procedure*: To a suspension of 1,1′-ferrocenedithiol (0.45 g, 1.8 mmol) in ethanol (90 ml) was added a solution of sodium hydroxide (0.18 ml of 20M** solution, 3.6 mmol) under stirring and bubbling of nitrogen. To the resulting red-orange solution was added a solution of the corresponding α,ω-dibromopolyether (1.8 mmol) in ethanol (3 ml). The solution was stirred for 4 h at room temperature under bubbling of nitrogen. After evaporating the solution, the residue was redissolved in benzene and filtered. The filtrate was condensed by an evaporator and charged on silica-gel column chromatography. Elution by toluene-ethyl acetate mixture gave **5** and **6**.

4-Oxa-1,7-dithia[7]ferrocenophane (5a). Red needles, 8%, mp 62—63 °C. Found: C, 52.70; H, 5.28%. Calcd for $C_{14}H_{16}OS_2Fe$: C, 52.51; H, 5.04%. MS (75 eV): *m/z* 320 (M^+, 100%). IR (KBr): 3100, 2940, 2850, 1420, 1120, 1035, and 807 cm^{-1}.

4,22-Dioxa-1,7,19,25-Tetrathia[7.7]ferrocenophane (6a). Orange needles, 30%, mp 112—113 °C. Found: C, 52.56; H, 5.09%. Calcd for $C_{28}H_{32}O_2S_4Fe_2$: C, 52.51; H, 5.04%. MS (75 eV): *m/z* 640 (M^+, 100%), 320 ($M^+/2$, 32%), and 304 (30%). IR (KBr): 3100, 2900, 2870, 1420, 1195, 1110, 1025, and 810 cm^{-1}.

4,7-Dioxa-1,10-dithia[10]ferrocenophane (5b). Orange oil, 26%. Found: C, 52.91; H, 5.44%. Calcd for $C_{16}H_{20}O_2S_2Fe$: C, 52.75; H, 5.53%. MS (75 eV): *m/z* 364 (M^+, 100%). IR (KBr): 3100, 2930, 2860, 1420, 1295, 1130, 1025, and 810 cm^{-1}.

4,7,25,28-Tetraoxa-1,10,22,31-tetrathia[10.10]ferrocenophane (6b). Orange oil, 12%. Found: C, 52.99; H, 5.60%. Calcd for $C_{32}H_{40}O_4S_4Fe_2$: C, 52.75; H, 5.53%. MS (75 eV): *m/z* 728 (M^+, 100%), 364 ($M^+/2$, 56%), and 304 (25%). IR (KBr): 3100, 2900, 2870, 1420, 1325, 1290, 1140, 1020, and 810 cm^{-1}.

4,7,10-Trioxa-1,13-dithia[13]ferrocenophane (5c). Orange oil, 63.8%. Found: C, 53.00; H, 6.42%. Calcd for $C_{18}H_{24}O_3S_2Fe$: C, 52.94; H, 5.92%. MS (75 eV): *m/z* 408 (M^+, 100%). IR (Neat): 3100, 2930, 2875, 1420, 1365, 1295, 1150—1100, 1030, 830, and 810 cm^{-1}.

4,7,10,28,31,34-Hexaoxa-1,13,25,37-tetrathia[13.13]ferroccenophane (6c). Orange cubes, mp 84—85 °C, 17.1%. Found: C, 53.10; H, 6.09%. Calcd for $C_{36}H_{48}O_6S_2Fe_2$: C, 52.94; H, 5.92%. MS (75 eV): *m/z* 816 (M^+, 100%) and 408 ($M^+/2$, 42%). IR (KBr): 3100, 2860, 1295, 1240, 1120, 835, and 820 cm^{-1}.

4,7,10,13-Tetraoxa-1,16-dithia[16]ferrocenophane (5d). Orange oil, 60.4%. Found: C, 52.81; H, 6.29%. Calcd for $C_{20}H_{28}O_4S_2Fe$: C, 53.10; H, 6.24%. MS (75 eV): *m/z* 452 (M^+, 100%). IR (Neat): 3100, 2925, 2870, 1420, 1360, 1295, 1150—1095, 1025, and 830 cm^{-1}.

The electronic, ^{1}H-NMR, and ^{13}C-NMR spectra of the compounds described above were summarized in Tables 1 and 2.

Method of Solvent Extraction. Extractability of polyoxathiaferrocenophanes **5** and **6** with metal cations was measured by the extraction method[9] which was the somewhat modified Pedersen method[16].

Measurement of the Electronic, ^{1}H- and ^{13}C-NMR Spectra in the Presence of Silver(I) Nitrate. The electronic spectra of **5b—d** (4.00×10^{-3}M) was recorded in the presence of silver(I) nitrate (2.00×10^{-3}M) in acetonitrile. The ^{1}H-NMR spectra of **5b—d** (0.08 mmol) was recorded in the presence of 0.25, 0.5, 1, 2, and 3 equivalents of silver(I) nitrate in acetonitrile-d_3 (*ca.* 0.3 ml). The results were summarized in Table 4 and Fig. 2. The ^{13}C-NMR spectra of **3b—d** and **8** (0.08 mmol) was recorded in the presence of silver(I) nitrate (0.1 mmol) in acetonitrile-d_3 (*ca.* 0.3 ml).

The Complex of 5c with Silver(I) Nitrate. **5c** (0.37 g, 0.9 mmol) and silver(I) nitrate (0.15 g, 0.9 mmol) were dissolved in acetonitrile (3 ml) under nitrogen. The resulting solution was heated for 3 min and then poured into anhydrous ether (40 ml). Yellow crystalline precipitates resulted.

Filtration and washing with anhydrous ether gave yellow crystals (0.43 g, 74%). The crystals were dissolved in chloroform and the resulting solution was filtered into anhydrous ether to give a pure complex. Mp 152 °C (decomp).

Found: C, 37.53; H, 4.32%. Calcd for $C_{18}H_{24}O_6NS_2FeAg$: C, 37.39; H, 4.18%. IR (KBr): 3090, 2870, 1390—1355, 1300, 1120, 1125, and 835 cm^{-1}.

**1 M=1 mol dm^{-3}.

References

1) R. M. Izatt and J. J. Christensen, "Synthetic Multidentate Macrocyclic Compounds," Academic Press, New York (1978).

2) C. J. Pedersen, *J. Org. Chem.*, **36**, 254 (1971).

3) W. Rosen and D. H. Busch, *Inorg, Chem.*, **9**, 262 (1970).

4) T. L. Jones, L. L. Zimmer, L. L. Diaddario, D. B. Rorabacher, and L. A. Ochrymowycz, *J. Am. Chem. Soc.*, **97**, 7163 (1975).

5) G. Oepen and F. Vögle, *Liebigs Ann. Chem.*, **1979**, 1094; A. P. Bell and C. D. Hall, *J. Chem. Soc., Chem. Commun.*, **1980**, 163.
6) A. Ratajczak and B. Czech, *Polish J. Chem.*, **54**, 57 (1980).
7) B. Czech and A. Ratajczak, *Polish J. Chem.*, **54**, 767 (1980).
8) J. F. Biernat and T. Wilczewski, *Tetrahedron*, **36**, 2521 (1980).
9) S. Akabori, Y. Habata, Y. Sakamoto, M. Sato, and S. Ebine, *Bull. Chem. Soc. Jpn.*, **56**, 537 (1982).
10) A preliminary report: M. Sato, M. Kubo, S. Ebine, and S. Akabori, *Tetrahedron Lett.*, **22**, 185 (1981).
11) J. J. Bishop, A. Davison, M. L. Katcher, D. W. Lichtenberg, R. E. Merrill, and J. C. Smart, *J. Organomet. Chem.*, **27**, 241 (1971).
12) L. N. Mulay and M. E. Fox, *J. Chem. Phys.*, **38**, 760 (1963)
13) D. R. Scott and R. S. Becker, *J. Chem. Phys.*, **35**, 516 (1961).
14) M. Sato, S. Tanaka, S. Ebine, K. Morinaga, and S. Akabori, to be submitted.
15) T. Ho, "Hard and Soft Acids and Bases Principle in Organic Chemistry," Academic Press, New York (1977).
16) C. J. Pedersen, *Fed. Proc.*, **27**, 1305 (1968).
17) C. J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017 (1967).
18) T. H. Barr and W. E. Watts, *Tetrahedron*, **34**, 6111 (1968).
19) K. R. Mann, W. H. Morrison, Jr., and D. N. Hendrickson, *Inorg. Chem.*, **13**, 1180 (1974).
20) A. Luttringhaus, F. Cramer, H. Prinzbach, and F. M. Henglein, *Justus Liebigs Ann. Chem.*, **613**, 185 (1958).
21) B. Dietrich, J. M. Lehn, J. P. Sauvage, and J. Blanzat, *Tetrahedron*, **29**, 1629 (1973).