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Crystal Structure and NMR Spectral Studies of Alkali Thiocyanate Complexes with Polyoxa[*n*]ferrocenophanes

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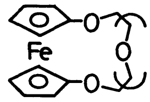
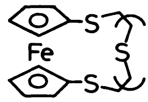
^{1}H- and ^{13}C-NMR spectra of free ligands and their alkali metal complexes with a new type of crown ethers containing a ferrocene unit have been recorded. The change of chemical shifts in ^{1}H- and ^{13}C-NMR spectra was attributed to an electronic field effect and a conformational change on the metal complexation, respectively. The crystal structure of the complex of 1,4,7,10,13-pentaoxa[13]ferrocenophane with sodium thiocyanate was determined by the X-ray method. The crystals are orthorhombic, space group Cccn, with a=20.579(4), b=25.622(8) c=7.606(1) Å, U=4010(2) Å^3, Z=8, D_c=1.48 g cm^{-3}. The distances between the iron atom of a ferrocene nucleus and the incorporated sodium cation and between the sodium cation and the nitrogen atom of a counter anion are 4.129 and 2.541 Å, respectively. The results suggest that the iron atom of the ferrocene does not take part directly in complex formation and that the sodium cation forms a contact ion pair with the nitrogen atom of a counter anion.

Polyoxa- and polythia[*n*]ferrocenophanes are a kind of crown ether-like compounds including a ferrocene subunit as a ring member; in it, the iron atom may act as a coordinatable heteroatom. Recently, several research groups have treated the interaction between the iron atom of ferrocene nucleus and the complexed cation,[1–3] and have synthesized polyoxa- and polythia[*n*]ferrocenophanes. Biernat *et al.* concluded that there is no interaction between the iron atom of **1a** and the complexed rubidium cation in methanol by only the UV spectral studies.[1] However, we ourselves previously observed a certain interaction between the iron atom of oxathia[*n*]ferrocenophane and the complexed silver cation.[4] In a previous paper,[5] we have reported the preparation and some spectroscopic and physicochemical properties of the polyoxa[*n*]ferrocenophanes and its alkali thiocyanate complexes. Polyoxa[*n*]ferrocenophanes (**1**) show a weak complexing ability to alkali, alkaline-earth cations (hard ions), and a higher complexing ability to silver and thallium cations (soft ions). It is of interest to know what kind of interaction can be expected between the iron atom of a ferrocene nucleus and the complexed cation. In continuation of our investigations about the complexes of polyoxaferrocenophanes with metal cations, we now report the ^{1}H-NMR, ^{13}C-NMR, and the crystal structure of the complexes of polyoxa[*n*]ferrocenophanes with alkali-metal thiocyanates.



1

1a : n=4
1b : n=3



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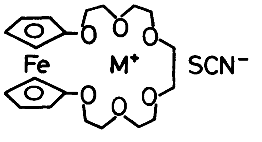
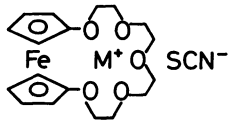


3

3a : M=Li
3b : M=Na
3c : M=K



4

4a : M=Li
4b : M=Na

Results and Discussion

Ligands (**1a** and **1b**) form complexes with various alkali metal thiocyanates.[5] Suitable crystals for the X-ray analysis of **4b** were obtained by slow addition of hexane to the chloroform solution containing the ligand and sodium thiocyanate.

^{1}H-NMR Spectra of the Complexes 3 and 4. In the ^{1}H-NMR spectrum of **1a**, the signals at δ 4.14 and 3.86 which appear as triplets (J=2.0 Hz) are attributable to α- and β-protons of cyclopentadienyl rings, respectively, while the two singlets at δ 3.70 and 3.78 and the two triplets at δ 3.86 and 4.05 (J=4.6 Hz) are attributable to the methylene protons of the macrocycle. The ^{1}H-NMR spectra of compounds **1** were compared with those of alkali metal thiocyanate complexes **3** and **4**. The chemical shift of the complexes are shown in Table 1, together with those of uncomplexed ligands (**1a** and **1b**). The differences in the chemical shifts between the free ligands and the complexes are also shown in parentheses in Table 1. The change of chemical shifts of the ferrocenophanes on complexation with alkali metals seems to be attributable to a) an electronic field effect caused by the metal cation and the counter anion, b) perturbation of the electron density on the carbon atom through M$^+$-Fe-cyclopentadienyl rings, and c) factors due to the conformational change on complexation. The downfield shift was observed not only on the methylene protons but also on all protons of the cyclopentadienyl rings of ferrocene nucleus. In **4a** and **4b**, the change of chemical shifts of the cyclopentadienyl ring protons seems to depend on the distance of each proton from the complexation site, that is, the downfield shift of α-protons is more enhanced than those of β-protons. By contrast, the chemical shift differences between α- and β-protons in **3a—c** were approximately the same. The cavity of the macrocyclic polyether ring of **1a** seems to be too large for Li$^+$ and Na$^+$, and the complexes may take a folded geometry as pictured by Poonia.[6] The above results are in good

Table 1. ^{1}H-NMR spectral data of compounds **1a** and **1b** and their alkali metal thiocyanate complexes[a,b]

Compd	Cp-ring protons		Methylene protons		
	Hα	Hβ			
1a	4.09(t)	3.82(t)	3.66(s)	3.68(s)	3.93—4.04 (m)
3a(LiSCN)	4.17(t) (+0.08)	3.92(t) (+0.10)	3.75(s) (+0.09)	3.72(s) (+0.04)	4.04—3.78 (m)
3b(NaSCN)	4.13(t) (+0.04)	3.85(t) (+0.03)	3.66(s) (±0.0)	3.71(s) (+0.03)	4.06—3.77 (m)
3c(KSCN)	4.14(t) (+0.05)	3.90(t) (+0.08)	3.74(s)	(*ca.* +0.10)	4.04—3.78 (m)
1b	4.11(t)	3.81(t)	3.68(s)	4.06—3.92 (m)	
4a(LiSCN)	4.31(t) (+0.20)	3.86(t) (+0.05)	3.76(s) (+0.08)	4.11—3.79 (m)	
4b(NaSCN)	4.41(t) (+0.30)	3.89(t) (+0.08)	3.71(s) (+0.03)	3.98—3.76 (m)	

a) Chemical shifts as δ values. A downfield shift is denoted as a positive value. b) Deuteriochloroform was used as solvent.

Table 2. ^{13}C-NMR spectral data of compounds **1a** and **1b** and their alkali metal thiocyanate complexes[a,b]

Compd	Cb	Cα	Cβ	Methylene carbons			
1a	127.1	56.2	61.9	71.2	70.6	70.1	
3a(LiSCN)	126.6 (−0.5)	56.8 (+0.6)	62.3 (+0.4)	70.6	70.5 (−0.1—−0.6)	70.4	70.0
3b(NaSCN)	126.2 (−0.9)	56.9 (+0.7)	62.5 (+0.6)	69.5	69.4 (*ca.* −0.7)		
3c(KSCN)	126.2 (−0.9)	57.3 (+1.1)	62.4 (+0.5)	71.1	70.2 (−0.1—−0.6)	69.5	
1b	126.9	56.4	61.9	71.3	70.7	70.3	70.0
4a(LiSCN)	125.0 (−21.9)	58.4 (+2.0)	63.0 (+1.1)	71.1	69.1 (−0.2—−1.6)	68.4	
4b(NaSCN)	124.9 (−2.0)	59.9 (+3.5)	63.6 (+1.7)	73.4	69.1 (+2.1—−3.0)	68.7	

a) Chemical shifts as δ values. A downfield shift is denoted as a positive value. b) Deuteriochloroform was used as solvent. c) Shift changes are presented in parentheses.

agreement with the hole size estimated from Corey-Pauling-Koltum stereomolecular model (**1a**: 2.8—3.4 Å and **1b**: 2.2 Å) with the ionic diameters[7] of Li^+ (1.20 Å), Na^+ (1.90 Å), and K^+ (2.66 Å). It has already been reported[8] that in an 18-membered crown ether, such as dibenzo-18-crown-6, the addition of more than one equivalent of KSCN caused no further chemical shift change, although the resonances of all protons were successively shifted until done equivalent of the metal salt was added. The above results suggest that the electronic field effect of the counter anion, SCN^-, on all the protons of the host crown ether is small and negligible. Therefore, the chemical shifts of the complexes seems to be best interpreted in terms of an electronic field effect due to the incorporated metal cation and a perturbation of the electron density on the carbon atom through the C-O bond due to the coordination of an oxygen atom to the metal cation.

^{13}C-NMR Spectra. It is well known[9] that ^{13}C-NMR chemical shifts are sensitive to conformational changes, and relatively less sensitive to perturbation such as solvent effect than proton chemical shifts are. Therefore, the ^{13}C-NMR spectra of compounds **1a**, **1b**, and their alkali thiocyanate complexes (**3a**—**c** and **4a**—**b**) were recorded using deuteriochloroform as solvent. These results are listed in Table 2. The changes of the chemical shifts of the complexes are also shown in Table 2 in parentheses. The carbon resonances of cyclopentadienyl ring were assigned according to the literature.[10] Methylene carbon resonances were not rigorously assigned. In the ^{13}C-NMR spectra of **1b** the bridgehead carbon, α- and β-carbons of the cyclo-

pentadienyl rings showed their resonances at 126.9, 56.4, and 61.9 ppm, respectively, together with methylene carbons at 71.3, 70.7, 70.3, and 70.0 ppm. However, the ^{13}C-NMR spectrum of lithium thiocyanate complex (**4a**) showed resonances at 125.0, 58.4 (C_α), and 63.0 (C_β) ppm, together with the resonances of methylene carbons at 71.1. 69.1, and 68.4 ppm. Contrary to the upfield shifts of the bridgehead carbon of cyclopentadienyl rings, the α- and β-carbon resonances were shifted downfield on the metal complexation. The methylene carbon resonances were also shifted upfield on complexation except for the one methylene carbon of **4a**. In particular, the bridgehead carbon, C_b and methylene carbons at 2- and 12-positions showed a remarkable shift.

However, the spectral changes were slight for the alkali metal complexes containing six oxygen atoms, **3**, compared with the shift changes of **4**. The large shifts of bridgehead, C_α and methylene carbons at 2- and 12-position may be attributed to a special conformational change in which two oxygen lobes point inward. The upfield shifts of the bridgehead and methylene carbons and the downfield shifts of C_α- and C_β- resonances are in fair agreement with the results of alkali metal thiocyanate complexes of benzo-crown ethers.[8]

*Crystal Structure of **4b**.* The molecular conformation and the coordinative aspects of the complex **4b** and the numbering are shown in Fig 1. Bond lengths and bond angles are summarized in Table 4. The complex can be divided into two parts: the roughly planar complexing unit containing O(1) through O(5) and the ferrocene unit. In the complexing unit, the bonding from the sodium ion to the ligand is directed to the five oxygen atoms and nitrogen atom of counter anion. The Na^+-O(1), -O(2), -O(3), -O(4), and -O(5) bond lengths are 2,439(10), 2.449(9), 2.474(10), 2.396(9), and 2.631(9) Å, respectively. These distances are in fair agreement with the sum of the ionic radius of Na^+ (0.95 Å) and the van der Waals radius of an oxygen atom (1.4 Å). Similar distances have found in the sodium complexes of dibenzo-18-crown-6[11] and 18-crown-6.[12] The distance between Na^+ and a nitrogen atom of a thiocyanate anion is 2.541(12) Å, which is slightly longer than the sum of the ionic radius of Na^+ (0.95 Å) and the van der Waals radius of a nitrogen atom (1.5 Å). Such results suggest that the sodium cation is coordinated by five coplanar oxygen atoms and a nitrogen atom of a thiocyanate anion, to give a contact ion pair. The interatomic O-O distances between adjacent oxygen atoms (mean, 2.73 Å) are appropriately equal to the sum (2.80 Å) of the van der Waals radius of an oxygen atom. Thus, the neighboring oxygen atoms are in contact with each other. The distance between the iron atom of a ferrocene nucleus and the incorporated sodium cation is 4.129(5) Å: this value is too long compared with the sum of the van der Waals radius of the iron atom and ionic radius of a sodium cation (0.95 Å). The result suggests that the iron atom of the ferrocene unit does not take part directly in complex formation, although we can not rule out some very weak interactions between the iron atom and the incorporated sodium cation.

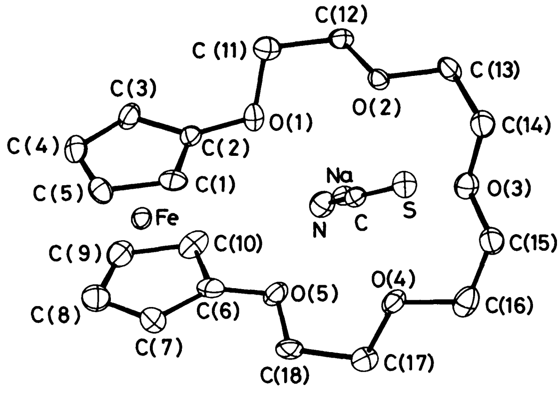


Fig. 1. Molecular structure of **4b** with atom numbering scheme.

Table 3. Fractional atomic coordinates ($\times 10^{-5}$), with estimated standard deviations in parentheses

Atom	x	y	z	$B_{eq}/Å^2$ a)
Na	55879(1)	11879(0)	18749(0)	3.0
N	53806(56)	12528(45)	-14110(151)	3.7
C	57022(56)	11971(43)	-26109(156)	2.4
S	61791(17)	11055(15)	-43583(49)	3.5
Fe	36373(8)	13426(6)	30355(23)	2.3
C(1)	39398(71)	10516(49)	6754(179)	3.3
C(2)	41081(57)	7038(45)	20679(196)	2.9
C(3)	35204(60)	5437(50)	29567(199)	3.4
C(4)	29971(60)	7968(52)	20409(195)	3.3
C(5)	32432(67)	11197(60)	6938(198)	3.8
C(6)	42977(69)	19024(50)	38353(188)	3.3
C(7)	37352(63)	21446(51)	31281(215)	3.7
C(8)	31886(79)	19702(62)	41905(245)	4.2
C(9)	34295(74)	16226(60)	54709(213)	4.3
C(10)	41332(70)	15595(56)	52664(174)	3.7
C(11)	48533(64)	271(49)	23712(173)	2.9
C(12)	55737(63)	-384(46)	26774(170)	2.9
C(13)	66238(62)	2048(50)	17051(195)	3.3
C(14)	69414(68)	6324(62)	5999(215)	4.0
C(15)	70194(70)	15541(61)	4615(228)	4.2
C(16)	67671(71)	20356(61)	14325(208)	4.2
C(17)	57772(63)	24754(55)	21654(172)	3.2
C(18)	50533(61)	23882(41)	21788(177)	2.9
O(1)	47254(40)	5666(35)	25541(141)	3.8
O(2)	59301(38)	2780(30)	15309(110)	2.6
O(3)	67750(42)	11187(37)	14141(119)	3.4
O(4)	60682(39)	20276(31)	13900(117)	2.9
O(5)	49233(40)	19551(32)	33088(119)	3.1

a) Equivalent isotropic temperature factor as defined by W. C. Hamilton (*Acta Crystallogr.*, **12**, 609 (1959)).

The C-C bond lengths of the cyclopentadienyl rings in the ferrocene unit were in the range of 1.410—1.444 Å in the A[C(1)-C(5)] ring and 1.409—1.465 Å in the B-[C(6)-C(10)] ring, with the average values of 1.432(48) Å and 1.437(47) Å, respectively. The valency angle in the A and B rings ranged over 107.0—110.3° and 104.2—111.2°, with the average values of 108.0(2)° and 108.0(2)°, respectively. The average length of the C-C bonds in the cyclopentadienyl rings is slightly longer than that found in ferrocene (1.40 Å)[13] but in good agreement with that of bridgehead ferrocenophanes.[14] The distance between the iron atom and the ring carbons ranged from 2.038 to 2.065 Å for the A ring and from 2.031 to 2.067 Å for the B ring; the average distance was 2.049 (30) Å for the A ring and 2.054(33) Å for the B ring. The perpendicular distances from the iron atom to the least square planes of the A and B rings, 1.647 and 1.651 Å, respectively, are both slightly longer than that found in ferrocene itself but agree well with those of some bridged ferrocenophanes.[14]

Table 4. Bond lengths and angles with estimated standard deviations in parentheses

Bond length	l/Å	Bond length	l/Å	Bond length	l/Å
Fe-C(1)	2.041(13)	C(4)-C(5)	1.410(21)	C(16)-O(4)	1.438(17)
Fe-C(2)	2.039(12)	C(6)-C(7)	1.419(20)	O(4)-C(17)	1.422(16)
Fe-C(3)	2.062(13)	C(7)-C(8)	1.455(22)	C(17)-C(18)	1.506(18)
Fe-C(4)	2.065(13)	C(8)-C(9)	1.409(23)	C(18)-O(5)	1.428(15)
Fe-C(5)	2.038(15)	C(9)-C(10)	1.465(21)	O(5)-C(6)	1.355(16)
Fe-C(6)	2.067(14)	C(10)-C(6)	1.439(19)	Na-O(1)	2.439(10)
Fe-C(7)	2.066(13)	C(2)-O(1)	1.369(15)	Na-O(2)	2.449(9)
Fe-C(8)	2.051(17)	O(1)-C(11)	1.413(16)	Na-O(3)	2.474(10)
Fe-C(9)	2.031(16)	C(11)-C(12)	1.510(19)	Na-O(4)	2.396(9)
Fe-C(10)	2.056(14)	C(12)-O(2)	1.398(15)	Na-O(5)	2.631(9)
Fe-Na	4.129(5)	O(2)-C(13)	1.445(15)	Na-N	2.541(12)
C(1)-C(2)	1.426(19)	C(13)-C(14)	1.527(21)	C-N	1.136(16)
C(1)-C(5)	1.444(30)	C(14)-O(3)	1.432(18)	C-S	1.668(12)
C(2)-C(3)	1.444(18)	O(3)-C(15)	1.422(19)		
C(3)-C(4)	1.437(19)	C(15)-C(16)	1.528(22)		

Bond angle	ϕ/°	Bond angle	ϕ/°	Bond angle	ϕ/°
C(1)-Fe-C(2)	40.9(1)	C(3)-Fe-C(9)	110.6(1)	C(1)-C(2)-C(3)	108.8(1)
C(1)-Fe-C(5)	41.5(1)	C(3)-Fe-C(10)	110.5(1)	C(2)-C(3)-C(4)	105.8(1)
C(1)-Fe-C(3)	69.3(1)	C(4)-Fe-C(5)	40.2(1)	C(3)-C(4)-C(5)	110.3(1)
C(1)-Fe-C(4)	68.0(1)	C(4)-Fe-C(6)	175.6(1)	C(4)-C(5)-C(1)	107.0(1)
C(1)-Fe-C(5)	41.5(1)	C(4)-Fe-C(7)	138.4(1)	C(7)-C(6)-C(10)	111.2(1)
C(1)-Fe-C(6)	108.2(1)	C(4)-Fe-C(8)	113.6(1)	C(6)-C(7)-C(8)	106.6(1)
C(1)-Fe-C(7)	111.3(1)	C(4)-Fe-C(9)	116.0(1)	C(7)-C(8)-C(9)	107.8(1)
C(1)-Fe-C(8)	143.1(1)	C(4)-Fe-C(10)	143.3(1)	C(8)-C(9)-C(10)	110.1(1)
C(1)-Fe-C(9)	174.2(1)	C(5)-Fe-C(6)	135.5(1)	C(9)-C(10)-C(6)	104.2(1)
C(1)-Fe-C(10)	132.3(1)	C(5)-Fe-C(7)	110.3(1)	C(1)-C(2)-O(1)	125.9(1)
C(2)-Fe-C(3)	41.2(1)	C(5)-Fe-C(8)	114.5(1)	C(3)-C(2)-O(1)	125.3(1)
C(2)-Fe-C(4)	68.1(1)	C(5)-Fe-C(9)	144.3(1)	C(2)-O(1)-C(11)	113.4(1)
C(2)-Fe-C(5)	69.4(1)	C(5)-Fe-C(10)	173.7(1)	O(1)-C(11)-C(12)	106.0(1)
C(2)-Fe-C(6)	110.5(1)	C(6)-Fe-C(7)	40.2(1)	C(11)-C(12)-O(2)	110.7(1)
C(2)-Fe-C(7)	139.8(1)	C(6)-Fe-C(8)	68.0(1)	C(12)-O(2)-C(13)	112.7(1)
C(2)-Fe-C(8)	175.7(1)	C(6)-Fe-C(9)	68.0(1)	C(13)-C(14)-O(3)	106.5(1)
C(2)-Fe-C(9)	135.4(1)	C(6)-Fe-C(10)	40.8(1)	C(14)-O(3)-C(15)	112.2(1)
C(2)-Fe-C(10)	106.2(1)	C(7)-Fe-C(8)	41.4(1)	O(3)-C(15)-C(16)	105.5(1)
C(3)-Fe-C(4)	40.8(1)	C(7)-Fe-C(9)	68.8(1)	C(16)-O(4)-C(17)	113.6(1)
C(3)-Fe-C(5)	69.5(1)	C(7)-Fe-C(10)	69.8(1)	C(17)-C(18)-O(5)	107.7(1)
C(3)-Fe-C(6)	140.7(1)	C(8)-Fe-C(9)	40.4(1)	C(18)-O(5)-C(6)	115.7(1)
C(3)-Fe-C(7)	178.9(1)	C(8)-Fe-C(10)	70.0(1)	C(10)-C(6)-O95)	120.5(1)
C(3)-Fe-C(8)	137.6(1)	C(2)-C(1)-C(5)	108.0(1)	C(7)-C(6)-O(5)	128.3(1)

It is well known[15] that the tilt angle between two cyclopentadienyl rings varies greatly with the number of bridging methylenes of the bridged ferrocenophanes. A deformation strain resulting from an interannular bridge shorter than four carbons in length can not be accomodated in the ferrocene nucleus without distortion of the prefered coplanar molecular geometry by the ring tilting. It is noteworthy that the cyclopentadienyl rings in the present complex (**4b**), containing thirteen atoms in an interannular bridge, deviates from planality, and its tilting angles are 3.30°. This may be because the crown ether part wrings the sodium cation. Finally it is also noteworthy that, although the nearest neighbor atoms between the intermolecules is C(11) and carbon atom of SCN$^-$ and the distance (3.34(17) Å) is roughly equal to the sum of the appropriate van der Waals radii, the smallest distance in the host molecule is C(18) and O(5) and this distance (3.41(18) Å) is longer than the sum of the van der Waals radii. These results suggest that there is no strong interaction between the intermolecules.

Experimental

Polyoxa[n]ferrocenophanes (**1a** and **1b**) and their alkali metal complexes (**3a**—**c** and **4a**, **b**) were prepared by the procedures described previously.[5] ^{1}H-NMR spectra (90 MHz) and the ^{13}C-NMR spectra (22.5 MHz) were recorded in deuteriochloroform with tetramethylsilane as an internal standard on a JEOL-FX-90Q spectrometer.

X-Ray Crystallography. A crystal of dimensions 0.4×0.4×0.1 mm, obtained from hexane-chloroform, was used for the intensity measurements. Intensity data were obtained on a Rigaku four-circle automatic difractometer, equipped with graphite-monochromated Mo $K\alpha$ radiation, and using the θ-2θ scan technique ($2\theta \leq 60°$). 2539 independent reflections ($F_o \geq 3.0\sigma F_o$) were corrected for Lorentz and polarization factors but not for absorption. The crystal data are as follows: $C_{19}H_{14}O_5FeNSNa$, mol wt 457.3, orthorhombic, space group Cccn, a=20.579(4), b=25.622(8), c=7.606(1) Å, U=4010(2) Å^3, Z=8, D_c=1.48 g cm^{-3}. The structure was solved by the direct methods. The positional and thermal parameters were refined by the block-diagonal least-squares methods. The final discrepancy index R is 0.10. The positional parameters for nonhydrogen atoms are listed in Table 3. Thermal parameters and observed and calculated structure factors are kept at the Chemical Society of Japan (Document No. 8352).

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