  Bull. Chem. Soc. Jpn., 61, 3565—3568 (1988)

Synthesis and Cation-Complexing Ability of Ferrocene or Ruthenocene Functionalized Crown Ethers Possessing 2,6-Pyridino Moieties

Taeko IZUMI,* Satoshi MURAKAMI, and Akira KASAHARA
Department of Applied Chemistry, Faculty of Engineering, Yamagata University, Yonezawa 992
(Received March 26, 1988)

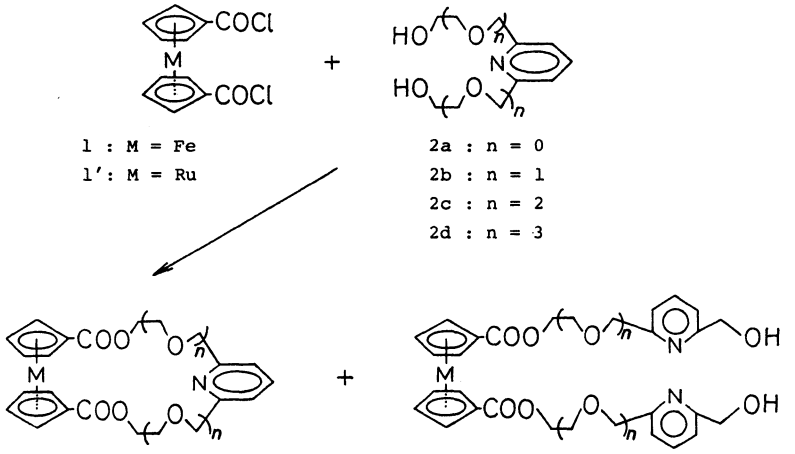
Keto crown ethers that contain ferrocene or ruthenocene and 2,6-disubstituted pyridine unit as part of the major ring have been reported. These keto crown ethers were synthesized by a reaction of 1,1′-metallocenedicarbonyl dichloride (ferrocene or ruthenocene) with 2,6-bis[ω-hydroxyoligo(oxyethylene)-α-ylmethyl]pyridine by using a high-dilution method. Their complexing ability with metal cations was measured by a solvent-extraction method, and was found to be poor with alkali metal cations but excellent with Ag^+, In^{3+}, and Zr^{4+} cations.

In view of the current interest in the functionality of crown ethers, many research groups have attempted investigations of new-type crown ethers[1] which contain sulfur or nitrogen atoms as well as heterocyclic or metallocene compounds and so on. We have previously described the synthesis and properties of ferrocene-incorporated keto crown ethers;[2] collected information indicates that the pyridyl unit in their crown ethers can be expected to be very efficient regarding cation extraction. Concerning macrocycles possessing subheterocyclic units, it has only been recently that these compounds have been shown to possess unique chemical and biochemical properties.[3] Furthermore, for the purpose of synthesizing crown compounds possessing specific properties, a number of ferrocene-incorporated crown ethers have already been reported; however, a crown ether containing a ruthenocene unit is rare.[4] We herein describe the preparation of multiheteromacrocycles that contain, as part of the major ring, metallocene (ferrocene or ruthenocene) and 2,6-disubstituted pyridine units combined with diester and $-OCH_2CH_2O-$ units, and their ability for forming complexes with various metal cations, including transition metals. In this work we considered (1) the influence of the pyridine unit depending on the ring size, and (2) the difference between ferrocene and ruthenocene on the complexing ability as a macrocycle.

Results and Discussion

Synthesis. Most of the hitherto reported macrocyclic diester compounds have been prepared by reactions between bis(acid chloride)s and diols in various yields, depending upon the ease of cyclization of substrates. In the present study, syntheses of **3** and **3′** were carried out in the presence of triethylamine by a modification of Bradshaw's method.[5]

Compounds **3a—d**, shown in Fig. 1, were prepared from 1,1′-ferrocenedicarbonyl dichloride **1** and an appropriate diol, **2a—d**. The dichloride (**1**) was generated from dicarboxylic acid with oxalyl dichloride in dichloromethane, and used immediately after extraction with hot hexane. Compound **3b**, for example,



3a: M = Fe, n = 0 3′a: M = Ru, n = 0 4a: M = Fe, n = 0 4′a: M = Ru, n = 0
3b: M = Fe, n = 1 3′b: M = Ru, n = 1 4b: M = Fe, n = 1 4′b: M = Ru, n = 1
3c: M = Fe, n = 2 3′c: M = Ru, n = 2 4c: M = Fe, n = 2 4′c: M = Ru, n = 2
3d: M = Fe, n = 3 3′d: M = Ru, n = 3 4d: M = Fe, n = 3 4′d: M = Ru, n = 3

Fig. 1.

was prepared as follows: the reaction was run under high-dilution techniques; **1** was added dropwise to 1.7 equivalents of **2b** at 80 °C for 15 hours then stirred for 24 hours to generate the crown ester compound **3b** (16%) together with 1,1′-ferrocenedicarbonyl-linked bis(pyridinemethanol) **4b** (34%). Furthermore, we initially intended a synthesis to binuclear ferrocenophane[2] using this **4b**; thus, this reaction mole ratio was not optimum for mononuclear ferrocenophane **3b**. An equimolar reaction and prolonged reaction times (36 h) at this esterification stage resulted in a yield of **3b** that approached 30%. The structural assignments for **3a—d** were based on spectral evidence and elemental analyses. The IR spectra of **3a—d** exhibit the characteristic absorption of an ester carbonyl (1715—1725 cm^{-1}), a pyridine ring (1590—1600, 1570—1585 cm^{-1}), and a 1,1′-disubstituted ferrocene ring (3100, 815—840 cm^{-1}).

In the ^1H NMR spectra, all of the pyridinoferrocenophanes (**3a—3d**) showed a similar pattern: ether OCH_2 groups at δ 3.99—3.70, ester $COOCH_2$ groups at δ 4.62—4.36, α-methylene protons of pyridine as sharp singlet at δ 5.36—4.62, α and β ring protons of the ferrocene as the A_2B_2 pattern at δ 4.92—4.77 and 4.43—4.38, and pyridine protons at δ 7.76—7.06. For example, the ^1H NMR spectrum of **3b** has seven signals: doublet of doublets at δ 4.40 and 3.99 for the methylene protons of bridges, two triplets centered at δ 4.77 and 4.43 for the ferrocene ring protons, a singlet at δ 4.86 for α-methylene protons of pyridine, a double doublet at δ 7.76 for γ-protons, and a doublet at δ 7.38 for β-protons of the pyridine ring, respectively. A distinct downfield shift for α-methylene protons of a pyridine ring, could be explained by a deshielding effect by the pyridine π face. The mass spectra and elemental analyses also confirmed the structures.

The case of pyridinoruthenocenophane (**3′a—3′d**) also afforded a similar result (see Table 1). The general procedure was conducted in an analogous manner to the synthesis of pyridinoferrocenophane, except for the substitution of 1,1′-ruthenocenedicarbonyl dichloride (**1′**) for 1,1′-ferrocenedicarbonyl dichloride (**1**). In the ^1H NMR spectral data for **3′a—3′d**, very little change in the chemical shifts for the β-protons and α-methylene protons of pyridine ring were observed.

Table 1. Reaction of 1,1′-Metallocenedicarbonyl Dichloride(M=Fe, Ru) with 2,6-Bis(ω-hydroxy substituted)pyridines(**2**)

Metallocene-dicarbonyl dichloride		Diol **2**	Product	Yield/%	Mp θ_m/°C
M=Fe	**1**	n=0	**3a**	9	240—242 (decomp)
			4a	19	Oil
	1	n=1	**3b**	16	114—115
			4b	34	Oil
	1	n=2	**3c**	18	76—77
			4c	30	Oil
	1	n=3	**3d**	12	Oil
			4d	21	Oil
M=Ru	**1′**	n=0	**3′a**	8	233—234
			4′a	45	Oil
	1′	n=1	**3′b**	20	124—125
			4′b	45	Oil
	1′	n=2	**3′c**	22	84—85
			4,c	40	Oil
	1′	n=3	**3′d**	12	Oil
			4′d	47	Oil

Extraction Ability. Concerning the influence of the functional parts of crown ethers toward the complexing ability, we already know the following. The introduction of carbonyl to crown ethers produces a product that is different from a simple crown ether. The characteristics include: 1) a destabilizing effect on the complex and/or 2) a reversal of the K^+-Ba^{2+} selectivity sequence, distinguishing features of naturally occurring antibiotic macrocycles.[6] Furthermore, complexes of a pyridine-incorporated cyclic polyether compound with Na^+, K^+, Ag^+, and Ba^{2+} showed unusual stabilities,[7] even though nitrogen-incorporated crown ethers caused a considerable drop in the stability of the K^+ complexes.[8] The complexing ability of the synthesized pyridinometallocenophanes were assessed by a solvent extraction of alkali, alkaline earth, and heavy-metal picrates with dichloromethane solutions of the ligands. The data are summarized in

Table 2. Extraction Data (Water-Dichloromethane)[a]

Compound	Extracted/%																
	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Al^{3+}	In^{3+}	Tl^+	Ce^{3+}	Ag^+	Hg^{2+}	Pb^{2+}	Zr^{4+}
3a	1.4	10.1	11.4	5.5	2.1	2.9	3.6	2.1	5.7	5.0	72.8	2.1	1.4	14.3	3.6	6.4	85.4
3b	4.0	4.6	5.4	9.9	3.7	3.6	3.1	3.1	5.1	24.5	85.7	5.6	7.7	84.0	4.3	8.9	90.1
3c	6.7	17.7	19.0	15.4	3.0	9.7	9.7	10.7	11.4	47.5	93.4	52.3	15.7	95.6	19.1	63.2	93.4
3d	11.5	11.5	44.6	26.6	2.1	10.3	9.3	24.5	14.1	10.4	88.1	74.9	2.6	96.0	22.1	43.1	88.1
3′a	1.4	0	1.4	1.0	1.1	1.4	1.0	0.7	1.0	5.0	60.7	1.4	1.4	17.9	4.3	1.0	69.3
3′b	1.4	0	0	1.4	1.0	1.4	1.4	1.4	0	5.0	61.4	2.8	1.0	59.0	4.3	2.9	72.0
3′c	1.4	1.4	2.1	2.9	2.9	4.3	4.3	3.6	1.4	11.4	81.4	21.0	3.9	91.0	6.4	40.0	84.3
3′d	1.4	1.4	4.2	2.9	1.0	1.4	2.6	1.4	0	11.7	80.4	17.8	1.4	86.4	7.1	30.7	84.3

a) Equal volumes of water and dichloromethane, and picric acid at 7.0×10^{-5} M(1M=1 mol dm^{-3}). Concentration of ferrocenophane: 7.0×10^{-4} M. Concentration of metal nitrate: 0.1 M.

Table 2. These two groups of pyridinometallocenophanes (M=Fe and Ru) showed a similar tendency regarding a low extractability toward alkali metal and alkaline earth metal cations, and a high extractability toward heavy-metal cations, in particular for Ag^+. Ferrocenophane, as a whole, however, showed a higher cation-binding ability compared to ruthenocenophane. For example, regarding the extractability toward a K^+ cation, **3a**, **3c**, and **3d** (M=Fe), expect **3b**, showed a moderate extractability and a similar K^+-Ba^{2+} selectivity sequence as was described above (due to an ester carbonyl); however, **3'a—3'd** (M=Ru) showed almost no extractability. These results indicate the distinction between ruthenium and iron(II) as the central metal of metallocene, as well as the cavity size. It is also interesting that the extraction ability of almost all pyridinometallocenophanes showed a remarkable dependence on the cavity size in the macrocycle of **3a—3d** and **3'a—3'd**; especially **3d** (n=3) and **3'c** (n=2) showed the best ability for Ag^+.

Furthermore, our original intention to introduce a pyridine moiety to metallocenophane in order to enhance the cation binding ability and selectivity has been accomplished. The effects of this pyridine are clear, compared with the results of the 1,1'-ferrocenyl keto crown ether, which we reported before.[2] A similar trend of affinity toward transition metal cations has been observed regarding hitherto reported "crowned" ferrocenophane as well as synthesized pyridinometallocenophanes; this suggests that the metal atom of the metallocene nucleus participates in the complexation process. It should be emphasized that all synthesized pyridinometallocenophanes are capable of forming stable complexes with silver (not an oxidative decomposition).

Experimental

Materials and Measurements. All melting points are uncorrected. 2,6-Bis(hydroxymethyl)pyridine, diethylene glycol, triethylene glycol were commercial products.

1,1'-Ferrocenedicarboxylic acid[9] and 1,1'-ruthenocenedicarboxylic acid[10] were prepared by methods described in the literature. The other reagents employed were commercial materials or were prepared by the usual methods. All inorganic compounds were reagents grade. The IR, ^{1}H NMR, and mass spectra were recorded on Hitachi 260-10, Hitachi R-22, and Hitachi RMU-6M spectrometers, respectively.

Synthesis of 2,6-Bis(ω-hydroxy substituted)pyridine (2) (n=1—3). Sodium 2-hydroxyethoxide was prepared from sodium methoxide (0.02 mol, 1.1 g) and dry ethylene glycol (0.05 mol, 3.1 g) in 20 cm^3 of ether with stirring at 40 °C for 4 h. Ether was removed in vacuo, and the residue was dissolved in 50 cm^3 of dry THF. To the solution, 2,6-bis(chloromethyl)pyridine (0.01 mol, 1.76 g) in 150 cm^3 of dry THF was added dropwise for 12 h at 55 °C; additional refluxing took place for 8 h. Sodium chloride salt was filtered off; the filtrate was then concentrated in vacuo, and the residue purified by silica-gel column chromatography. The first fraction yielded unreacted ethylene glycol; the second fraction gave 1.8 g (80%) of diol **2b** (n=1) as a pale-yellow viscous oil.

Diols **2c** (n=2) and **2d** (n=3) were also prepared by the above-mentioned procedure, except that diethylene glycol and triethylene glycol were used as a substitute for ethylene glycol, respectively. Along with unreacted diethylene glycol and triethylene glycol, the major isolated fraction was diol **2c** (74%) and **2d** (75%) as a pale-yellow viscous oil, respectively.

2,6-Bis[(2-hydroxy)methyl]pyridine (2b).[11] **2,6-Bis[[2-(2-hydroxyethoxy)ethoxy]methyl]pyridine (2c).** IR (neat) 3430—3350, 2930—2860, 1600, 1580 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=3.63—3.72 (m, -C<u>H</u>$_2$-C<u>H</u>$_2$-, 16H), 3.83 (s, -O<u>H</u>, 2H), 4.66 (s, Py-C<u>H</u>$_2$-, 4H), 7.35 (d, 3,5-Py<u>H</u>, 2H, J=8 Hz), 7.72 (d-d, 4-Py<u>H</u>, 1H, J=8 and 9 Hz). MS (70 eV) m/z 315 [M$^+$].

2,6-Bis[[[2-(2-hydroxyethoxy)ethoxy]ethoxy]methyl]pyridine (2d). IR (neat) 3400, 2900—2850, 1570, 1590 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=2.85 (br-s, -O<u>H</u>, 2H), 3.70—3.75 (m, -C<u>H</u>$_2$C<u>H</u>$_2$-, 24H), 4.68 (s, Py-C<u>H</u>$_2$-, 4H), 7.37 (d, Py-<u>H</u>, 2H, J=8 Hz), 7.73 (d-d, Py-<u>H</u>, 1H, J=8 and 9 Hz). MS (70 eV) m/z 403 [M$^+$].

Synthesis of 3a—d and 3'a—d. General Procedure. 1 was prepared from 1,1'-ferrocenedicarboxylic acid and oxalyl dichloride by a method described in the literature.[12] Under an atmosphere of nitrogen, to a solution of **1** (2.2 g, 7 mmol) and triethylamine (1.2 g, 12 mmol) in dry benzene (150 cm^3), diol **2** (n=0—3) (12 mmol) diluted with dry benzene (100 cm^3) and dry THF (50 cm^3) was added dropwise over 15 h with stirring. An additional 24 h period of gentle refluxing followed. After removing the solvent under reduced pressure, the residue was purified by silica-gel column chromatography. The first fraction eluted with benzene or chloroform gave pyridinoferrocenophane (**3a—d**); the second fraction eluted with chloroform-methanol (20 : 1) gave 1,1'-ferrocene dialcohol (**4a—d**) as a reddish oil. The crude product was recrystallized from benzene-hexane.

Pyridinoruthenocenophane (**3'a—d**) was also prepared by a reaction of **1'** (1.1 g, 3.1 mmol) and diol **2** (n=0—3) (6.2 mmol) through the above-mentioned method. The results are summarized in Table 1.

2,11-Dioxa[3](2,6)pyridino[3](1,1')ferrocenophane-1,12-dione(3a).[2] **2,5,14,17-Tetraoxa[6](2,6)pyridino[6](1,1')ferrocenophane-1,18-dione (3b).** IR(KBr) 3105, 2990, 2850, 1715, 1600, 1580 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=3.99 (d-d, 4H, -C<u>H</u>$_2$C<u>H</u>$_2$- J=4 and 7 Hz), 4.40 (m, 4H, -COOC<u>H</u>$_2$-), 4.43 (t, 4H, Fc-<u>H</u>$_\beta$, J=4.5 Hz), 4.77 (t, 4H, Fc-<u>H</u>$_\alpha$, J=4.5 Hz), 4.86 (s, 4H, Py-C<u>H</u>$_2$-), 7.38 (d, 2H, 3,5-Py<u>H</u>, J=8 Hz), 7.76 (d-d, 1H, 4-Py<u>H</u>, J=8 and 9 Hz). MS (70 eV) m/z 465 [M$^+$]. Found: C, 59.31; H, 4.93%. Calcd for $C_{23}H_{23}FeNO_6$: C, 59.37; H, 4.98%; M, 465.29.

2,5,8,17,20,23-Hexaoxa[9](2,6)pyridino[9](1,1')ferrocenophane-1,24-dione (3c). IR(KBr) 3105, 2960—2870, 1725, 1600, 1580 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=3.77 (br-s, 12H, -C<u>H</u>$_2$OC<u>H</u>$_2$C<u>H</u>$_2$-), 4.30—4.42 (m, 8H, -COOC<u>H</u>$_2$-+Fc-<u>H</u>$_\beta$), 4.67 (s, 4H, Py-C<u>H</u>$_2$-), 4.77 (t, 4H, Fc-<u>H</u>$_\alpha$, J=4.5 Hz), 7.35 (d, 2H, 3,5-Py<u>H</u>, J=8 Hz), 7.68 (d-d, 1H, 4-Py<u>H</u>, J=8 and 9 Hz). MS (70 eV) m/z 553 [M$^+$]. Found: C, 58.64; H, 5.61%. Calcd for $C_{27}H_{31}FeNO_8$: C, 59.60; H, 5.64%; M, 553.39.

2,5,8,11,20,23,26,29-Octaoxa[12](2,6)pyridino[12](1,1')-ferrocenophane-1,30-dione (3d). IR (neat) 3100, 2970—2880, 1720, 1600, 1585 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=3.70 (br-s, 20H, -C<u>H</u>$_2$OC<u>H</u>$_2$C<u>H</u>$_2$OC<u>H</u>$_2$C<u>H</u>$_2$-), 4.36 (m, 8H, -COOC<u>H</u>$_2$-+Fc-<u>H</u>$_\beta$), 4.62 (s, 4H, Py-C<u>H</u>$_2$-), 4.79 (t, 4H, Fc-<u>H</u>$_\alpha$, J=4.5 Hz), 7.35 (d, 2H, 3,5-Py<u>H</u>, J=8 Hz), 7.65 (d-d, 1H, 4-Py<u>H</u>, J=8

and 9 Hz). MS (70 eV) m/z 641 [M^+]. Found: C, 58.10; H, 6.09%. Calcd for $C_{31}H_{39}FeNO_{10}$: C, 58.04; H, 6.13%; M, 641.50.

2,11-Dioxa[3](2,6)pyridino[3](1,1')ruthenocenophane-1,12-dione (3'a). IR (KBr) 3100, 2930, 1720, 1600, 1585, 1295, 1150 cm^{-1}. ^1H NMR ($CDCl_3$) δ=4.72 (t, 4H, Rc-H$_\beta$, J=4.5 Hz), 5.32 (s, 8H, Rc-H$_\alpha$+Py-CH$_2$-), 7.04 (d, 2H, 3,5-PyH, J=8 Hz), 7.63 (d-d, 1H, 4-PyH, J=8 and 9 Hz). MS (70 eV) m/z 422 [M^+]. Found: C, 54.07; H, 3.61%. Calcd for $C_{19}H_{15}RuNO_4$: C, 54.03; H, 3.58%; M, 422.40.

2,5,14,17-Tetraoxa[6](2,6)pyridino[6](1,1')ruthenocenophane-1,18-dione (3'b). IR (KBr) 3100, 2950—2860, 1715, 1590, 1570, 1275, 1145 cm^{-1}. ^1H NMR ($CDCl_3$) δ=3.85 (d-d, 4H, -CH$_2$O-, J=5 and 8Hz), 4.28 (d-d, 4H, -COOCH$_2$-, J=5 and 8 Hz), 4.70 (t, 4H, Rc-H$_\beta$, J=4.5 Hz), 4.76 (s, 4H, Py-CH$_2$-), 5.08 (t, 4H, Rc-H$_\alpha$, J=4.5 Hz), 7.34 (d, 2H, 3,5-PyH, J=8 Hz), 7.74 (d-d, 1H, 4-PyH, J=8 and 9 Hz). MS (70 eV) m/z 510 [M^+]. Found: C, 54.06; H, 4.57%. Calcd for $C_{23}H_{23}RuNO_6$: C, 54.11; H, 4.54%; M, 510.51.

2,5,8,17,20,23-Hexaoxa[9](2,6)pyridino[9](1,1')ruthenocenophane-1,24-dione (3'c). IR (KBr) 3070, 2940—2840, 1715, 1590, 1570, 1275, 1135 cm^{-1}. ^1H NMR ($CDCl_3$) δ=3.65—3.80 (br-s, 12H, -CH$_2$OCH$_2$CH$_2$O-), 4.28 (d-d, 4H, -COOCH$_2$-, J=5 and 6 Hz), 4.66 (t, 4H, Rc-H$_\beta$, J=4.5 Hz), 4.69 (s, 4H, Py-CH$_2$-), 5.06 (t, 4H, Rc-H$_\alpha$, J=4.5 Hz), 7.35 (d, 2H, 3,5-PyH, J=8 and 9 Hz), 7.69 (d-d, 1H, 4-PyH, J=8 and 9 Hz). MS (70 eV) m/z 598 [M^+]. Found: C, 54.15; H, 5.27%. Calcd for $C_{27}H_{31}RuNO_3$: C, 54.17; H, 5.21%; M, 598.62.

2,5,8,11,20,23,26,29-Octaoxa[12](2,6)pyridino[12](1,1')-ruthenocenophane-1,30-dione (3'd). IR (neat) 3100, 2950—2850, 1720, 1595, 1580, 1280, 1150 cm^{-1}. ^1H NMR ($CDCl_3$) δ=3.74 (br-s, 20H, -CH$_2$OCH$_2$CH$_2$OCH$_2$CH$_2$O-), 4.30 (d-d, 4H, -COOCH$_2$-, J=5 and 6 Hz), 4.66 (s, 4H, Py-CH$_2$-), 4.70 (t, 4H, Rc-H$_\beta$, J=4.5 Hz), 5.14 (t, 4H, Rc-H$_\alpha$, J=4.5 Hz), 7.34 (d, 2H, 3,5-PyH, J=8 Hz), 7.71 (d-d, 1H, 4-PyH, J=8 and 9 Hz). MS (70 eV) m/z 686 [M^+]. Found: C, 54.19; H, 5.71%. Calcd for $C_{31}H_{39}RuNO_{10}$: C, 54.22; H, 5.72%; M, 686.72.

Solvent Extraction Experiments of Metal Ions. The extraction ability of synthesized polyoxapyridinometallocenophanes with metal picrates was examined by a method described in a previous paper.[2)]

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