

Figure 3. Chromatograms of Hg(II)-TODABE complex. Mobile phase; 0.010 M 1-OSANa and 0.0002 M(A), 0.0003 M(B), 0.0010 M(C), 0.0030 M(D, E, F) BTMACl in 40% MeOH(v/v), pH 5.5. Sample; 20 µg of Hg(II)(A), 10 µg of Hg(II)(B, C), 5 µg of Hg(II) (D) in 10 µL of aqueous solution, 5 µg of Hg(II) in 10 µL of artificial sea water (E) and industrial waste water (F). S₁ and S₂: system peaks.

Table 2. Recovery of Hg(II) ion spiked in artificial sea water and industrial waste water

Sample	Number	Hg(II) injected, µg	Hg(II) determined, µg ^a	Recovery, %
Hg(II) spiked	1	4.00	3.88	97.0±3.5
artificial sea water	2	7.00	7.05	100.7±2.3
	3	10.00	10.30	103.0±4.2
Cd(II), Cu(II),	1	4.00	3.80	97.5±4.5
Pb(II), Zn(II)	2	7.00	7.20	103.0±2.8
spiked industrial waste water	3	10.00	9.60	96.0±4.5

^a Average of triplicate determinations.

second system peak (S₂ in Figure 3).¹⁰

Determination of spiked mercury(II) ion in artificial sea water and industrial waste water. The artificial sea water spiked with the mercuric ion and industrial waste water spiked with Cd(II), Cu(II), Pb(II), Zn(II), Fe(III), and Hg(II) ions were treated with standard procedures and injected in the HPLC system. One of the results is shown in Figure 3(E, F) and analyses of spiked Hg(II) ion in artificial sea water and industrial waste water are shown in Table 2 for 3 different concentrations of spiked Hg(II). The recovery percentages of Hg(II) in each sample ranged from 96% to 103% and R.S.D. values were 2.8-4.5%.

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Structure-Specific Cleavage of Yeast tRNA^{phe} by (η⁶-mesitylene) manganese(I) tricarbonyl hexafluorophosphate

Sangbumn Kim, Younghoon Lee[†], and Inwon Park*

*Department of Chemistry,
Seoul National University,
Seoul 151-742, Korea*
[†]*Department of Chemistry,
Korea Advanced Institute of
Science and Technology,
Taejon 305-705, Korea*

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Determination of the tertiary structure of RNA molecule is essential in understanding its biological function. Recently, several synthetic redox-active coordination complexes have been used as chemical nucleases in probing the secondary and tertiary structures of nucleic acids.¹ Some of these complexes exhibit structure-specific cleavage patterns. 1,10-phenanthroline copper(I) [(OP)₂-Cu(I)], for example, exhibits a strong scission preference for the single-stranded loops of stem-loop structure in tRNA²; methidium propyl-EDTA iron (II) [MPE-Fe(II)] has a reactivity pattern with tRNA that is complementary to (OP)₂-Cu(I), preferring double-stranded regions.³ Recently, we have shown that MPE-Fe(II) exhibits a scission preference for terminal regions of helices and/or for unstable helical regions of 5S rRNA.⁴

Here we report that an octahedral coordination complex (η⁶-mesitylene) manganese(I) tricarbonyl hexafluorophosphate [MTH-Mn(I)]⁵ exhibits a structure-specific cleavage

*To whom correspondence should be addressed.

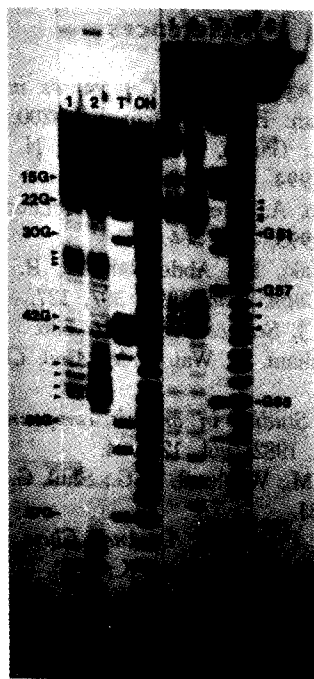


Figure 1. 12% polyacrylamide gel electrophoresis fractionation of the 3'-end labelled yeast tRNA^{Phe} after MTH-Mn(I)-induced cleavage. Prior to cleavage reaction, tRNA was renatured in a buffer containing 25 mM Tris-HCl, 100 mM NaCl, and 5 mM MgCl₂. Cleavage reaction was carried out in the presence of 7 mM H₂O₂ and 7 mM mercaptopropionic acid at 25 °C for 5 minutes (lane 1) and for 15 minutes (lane 2). Lanes T1, OH, and C indicate RNase T1 digestion, alkaline ladder, and incubation control, respectively.

pattern in yeast tRNA^{Phe} (Figure 1). The cleavage pattern of MTH-Mn(I) is represented on the backbone of yeast tRNA^{Phe} (Figure 2). Figure 2 shows that the sites 15, 16, 17, 18, 19, 20, 21, 22, 46, 47, 48, 49, 58, 59, and 60 are strongly cleaved, while the sites 33, 34, 35, and 43 are weakly cleaved. It is interesting to notice that MTH-Mn(I) preferentially cleaves along the sequences forming the corner of L structure and also cleaves, though weakly, the single-stranded anticodon loop. The L structure is formed by T loop, D loop, and variable loop of tRNA. It is known that the conformation of the pocket and that of the anticodon loop are well stabilized by the binding of hydrated magnesium ions as well as by the base-stackings.⁶ MTH-Mn(I) does not cleave the single-stranded region of acceptor end of tRNA, in spite of the fact that all of its bases, except for the 3' end, are base-stacked.

Our experimental results show that MTH-Mn(I) exhibits, much like (OP)₂-Cu(I) does, a prominent scission preference for the sequences constituting the single-stranded loops in the secondary structure of tRNA^{Phe}, whereas it exhibits very weak scission preference for the double-stranded stems, except that the anticodon stem is cleaved at G43 to a substantial extent. This finding suggests that an octahedral compound MTH-Mn(I) binds to tRNA molecule not by intercalating between the perfect base pairs, but rather by fitting at the sites in a pocket-like structure or in a stabilized hair-

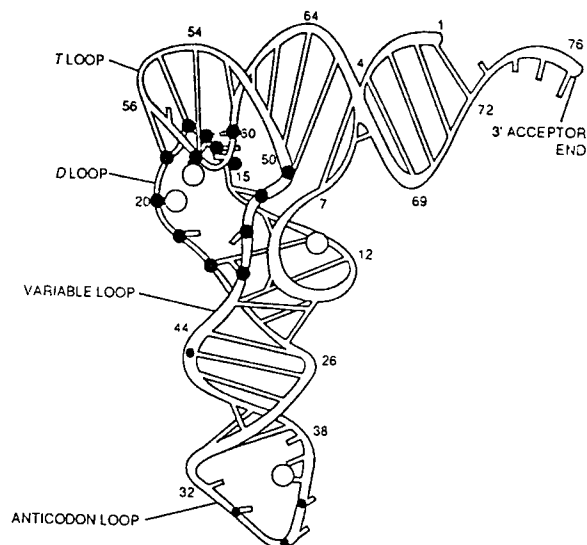


Figure 2. Diagrammatic representation of MTH-Mn(I)-induced cleavage pattern on the backbone of yeast tRNA^{Phe}. Large filled circles indicate strong cleavage and small filled circles indicate weak cleavage. The other sites are either not cleaved or very weakly cleaved at the most. Binding sites of hydrated magnesium ions are indicated by the open circles.

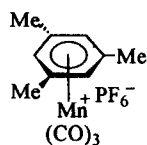
pin loop. We can see from Figure 1, however, that, as the reaction proceeds longer, double-stranded stems gradually become more scissile. We presume that the possible conformational changes occurring during the cleavage around the pocket and on the sequestered loop trigger the gradual structural disorganization of the stems of RNA, and this in turn makes the stems scissile to MTH-Mn(I).

The arguments presented above indicate that MTH-Mn(I) can be utilized as a useful chemical nuclease for searching the structural elements derived from the single-stranded regions of secondary structure of tRNA involved in the formation of a pocket in RNA molecules, and also for searching the loops stabilized by base-stackings in themselves.

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Novel Acyclic Polyethers Bearing Amide End-Groups and Their Complexation Studies in ISE

Jong Seung Kim*, Akira Ohki†, Nam Sook Cho‡, Ill Yong Yu, Takashi Hayashita§, and Shigeru Maeda†

Department of Chemistry, Konyang University,
Nonsan 320-800, Korea

†Department of Applied Chemistry &
Chemical Engineering, Faculty of Engineering,
Kagoshima University, Kagoshima 890, Japan

‡Department of Chemistry,
Chungnam National University,
Taejeon, 305-764, Korea

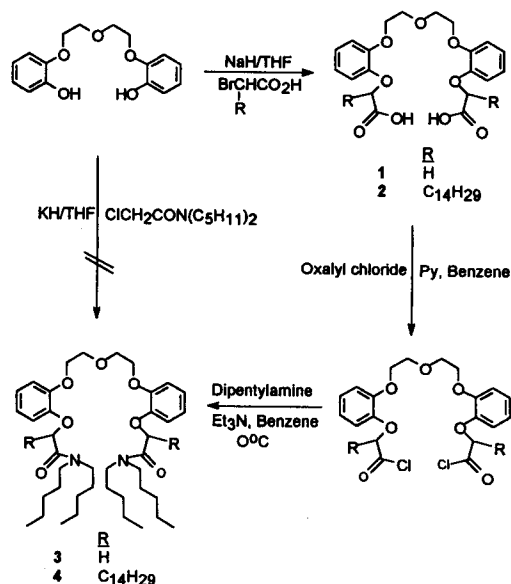
§Department of Chemistry, Saga University,
Honjo, Saga 840, Japan

Received June 10, 1996

Due to their complexation abilities with alkali, alkaline earth, and transition metals, a number of macrocyclic polyethers has been synthesized and employed for the separation of those metal ions.¹⁻³ Especially, complexation of metal ion with potential neutral chelating functions in the side arms have been well studied.⁴ Complexation studies with many natural ionophores such as valinomycin for potassium ion,⁵ monencin for sodium ion,⁶ and nonactin for ammonium ion⁷ have been well known. Potentiometric selectivities of solvent polymeric membrane electrodes containing structural derivatives of dibenzo-16-crown-5-oxyacetamides for sodium ion have been determined.⁸ Especially, selective separation of heavy metal ions such as Pb^{2+} and Cd^{2+} from industrial waste has long been considered as one of the most challenging problems remained in our environments.^{9,10} Therefore, much attention is now being paid to the recovery of and the detection of lead ion.

Complexation of acyclic dicarboxylic acid in which *n*-tetradecyl is replaced by *n*-hexyl group as a lipophilic side chain as denoted in Scheme 1 has shown an excellent selectivity for Pb^{2+} over Cu^{2+} in solvent extraction and in membrane transport experiment.¹¹ For solid state Pb^{2+} selective electrodes based on insoluble salts such as PbS , the presence of Cu^{2+} greatly interferes with the response of Pb^{2+} .¹² In addition,

*To whom correspondence should be addressed.



Scheme 1. Synthetic Routes for the Preparation of Acyclic Polyether Amides **3** and **4**.

tion, several Pb^{2+} selective electrodes based on stannous hexacyanoferrate (III)¹³ and titanium arsenate¹⁴ have been reported and exhibited $\log K_{Pb,Cu}^{Pot}$ values of 0.4 and -1.5 , respectively. Simon *et al.* reported a type of ionophore containing amide end-group which exhibits selectivities for $PbOH^+$, but poor selectivity for Pb^{2+} .¹⁵

Therefore, to enhance the selectivity for Pb^{2+} ion over other metal ions and to study the influence of nonionizable amide side arms and their lipophilicity on the complexation behavior by use of ISE system, herein we report that the synthetic methods for new compounds **3** and **4** which has pendant lipophilic side chains (*n*- $C_{14}H_{29}$) and results for the selective complexation of compound **3** and **4** with Pb^{2+} over other metal ions in ISE system.

Experimental

Chemical Analysis. IR spectra were obtained with a Perkin-Elmer 1600 Series FT-IR on potassium bromide pellet and are recorded in wave number. ¹H NMR spectra were recorded with an AF-300 spectrometer with the chemical shifts (δ) reported downfield from the internal standard, tetramethylsilane. Elemental analysis was performed by Vario EL Elemental Analyzer in Korea Basic Science Institute in Seoul, Korea.

Chemicals. Unless specified otherwise, reagent grade reactants and solvents were obtained from chemical suppliers and used as received. Dry solvents were prepared as follows: benzene and pentane were stored over sodium ribbon; dichloromethane was freshly distilled from lithium aluminium hydride. 1,5-Bis[2-(carboxymethoxy)phenoxy]-3-oxapentane (**1**) and 1,5-bis[2-(2'-carboxypentadecyloxy)phenoxy]-3-oxapentane (**2**) are known compound.¹⁶ Poly(vinyl chloride) (PVC) with an average polymerization degree of 1,100 was purchased from Waco Pure Chemical Industries. *o*-Nitrophenyloctyl ether (NPOE) and potassium tetrakis(*p*-chlorophenyl) borate (KTpCIPB) were obtained from Dojindo Lab. Deioni-