be abstracted by rhodium in **7**. Greater formation of hydrogenation products with **2** than that with **1** (Table 1) is explained in the same manner as discussed for isomerization above.

Finally, it should be mentioned that it is also possible to obtain a small amount of the carbonyl compounds (Table 1) *via* the allyhydridorhodium(III) intermediate even under hydrogen.

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Template Synthesis and Properties of Square Planar Nickel(II) and Copper(II) Complexes of 14-Membered Hexaaza Macrocyclic Ligands with Various Alkyl Pendant Arms at the Uncoordinated Nitrogens

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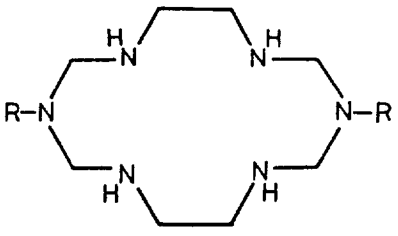
Square planar nickel(II) and copper(II) complexes of 14-membered macrocyclic ligands containing various alkyl pendant arms at the uncoordinated nitrogen atoms, 1,8-dipropyl, 1,8-dibutyl, 1,8-bis(2-methylpropyl), 1,8-bis(2-ethylhexyl), and 1,8-dibenzyl-1,3,6,8,10,13-hexaazacyclotetradecane have been prepared from the template condensation of ethylenediamine, formaldehyde, and appropriate primary amines in the presence of the metal ion. The spectroscopic and electrochemical properties of these complexes are similar to those of tetraaza macrocyclic complexes and are not affected significantly by the nature of the alkyl groups.

Introduction

Metal template syntheses often provide selective routes toward the products that are not obtainable in the absence of metal ion. Especially, template reactions involving formaldehyde and amines facilitate the preparation of saturated polyaza multidentate, macrocyclic, and macropolycyclic complexes.[1-7] The reactions are simple ("one pot reaction"), cheap, and high yielding.

Previously, we synthesized Ni(II) and Cu(II) complexes of fully saturated 14-membered hexaaza macrocyclic ligands A and B from the template condensation reaction of ethylenediamine, formaldehyde, and appropriate primary amines, and compared their properties with those of tetraaza macrocyclic complexes.[5] Although it has been known that number of methyl groups at the carbon or nitrogen atoms of the tetraaza macrocyclic ligands affect the spectra and the electrochemical properties of the complexes,[8-16] the effects of the nature of the alkyl groups on the properties of the complexes have rarely been studied. Therefore, we have been interested in the syntheses and comparison of the preoperties for the complexes of macrocyclic ligands C-G, 1,8-dipropyl, 1,8-dibutyl, 1,8-bis(2-methylpropyl), 1,8-bis(2-ethylhexyl), and 1,8-dibenzyl-1,3,6,8,10,13-hexaazacyclotetradecane, that contain various alkyl groups at the uncoordinated nitrogen atoms.



A: $R = CH_3$. B: $R = CH_2CH_3$. C: $R = CH_2CH_2CH_3$. D: $R = CH_2CH_2CH_2CH_3$. F: $R = CH_2CH(CH_3)_2$. F: $R = CH_2CH(CH_2CH_3)CH_2CH_2CH_2CH_3$. G: $R = CH_2C_6H_5$.

Experimental

Materials. All chemicals and solvents used in synthesis were of reagent grade and were used without further purification. Solvents used in spectral measurements were purified according to the literature method.[17]

Physical Measurements. Infrared spectra of the complexes were recorded on a Shimadzu IR-440 spectrophotometer. Conductance measurements were performed by using a Metrohm Herisau Conductometer E518 and RC-216B_2 conductivity bridge. Electronic absorption spectra were obtained on a Perkin Elmer Lambda 5 UV/vis spectrophotometer. ^1H and ^{13}C-NMR spectra were recorded using a Brucker WP 80 FT NMR spectrometer. Elemental analyses were performed by Instrumental Analysis Center, Seoul National University, Seoul. Cyclic Voltammetry was carried out with a Yanaco Voltammetric Analyzer P-1000 equipped with a FG-121B function generator and a Watanabe X-Y recorder. The electrochemical data were obtained in acetonitrile with 0.1 M $(n\text{-}Bu)_4NClO_4$ as supporting electrolyte. The working electrode was a platinum disk, the auxiliary electrode was a coiled platinum wire, and the reference electrode was SCE.

Synthesis. [Ni(C)](ClO$_4$)$_2$. To a stirred methanol solution (50 ml) of $NiCl_2 \cdot 6H_2O$(11.9 g) were slowly added 99% ethylenediamine (6.8 ml), 36% formaldehyde (20.6 ml), and 99% *n*-propylamine (4.2 ml). The mixture was heated at reflux for 24 h until a dark orange solution resulted, and filtered to remove nickel hydroxide. Excess perchloric acid was added dropwise to the filtrate with stirring, and the mixture was kept in a refrigerator until yellow precipitates formed. The yellow precipitates were filtered, washed with methanol, and air-dried. The precipitates were recrystallized from hot water. Yield: ~30%. *Anal.* Calcd for $NiC_{14}H_{34}N_6Cl_2O_8$: C, 30.87; H, 6.25; N, 15.44. Founa: C, 30.71; H, 7.22; N, 15.68.

[Ni(D)](ClO$_4$)$_2$·H$_2$O. This compound was prepared by a method similar to that for $[Ni(C)](ClO_4)_2$ except that 99% *n*-butylamine (10 ml) was used instead of *n*-propylamine. The yellow crystals formed were recrystallized from mixture of water and acetonitrile (5:1). Yield: ~25%. *Anal.* Calcd for $NiC_{16}H_{40}N_6Cl_2O_9$: C, 32.59; H, 6.78; N, 14.23. Found: C, 32.91; H, 6.12; N, 14.09.

[Ni(E)](ClO$_4$)$_2$·H$_2$O. To a stirred methanol solution (50 ml) of $NiCl_2 \cdot 6H_2O$(11.9 g) were slowly added 99% ethylenediamine (6.8 ml), 36% formaldehyde (20.6 ml), and 98% *iso*-butylamine (5.0 ml). The mixture was heated at reflux for 24 h. The solution was cooled to room temperature, and then water (20 ml) and excess perchloric acid were added to the solution. The solution was allowed to stand in a refrigerator until yellow precipitates formed. The precipitates were filtered, washed with methanol, and air-dried. The precipitates were recrystallized from a 1:1 mixture of water-acetonitrile. Yield: ~20%. *Anal.* Calcd for $NiC_{16}H_{40}N_6Cl_2O_9$: C, 32.59; H, 6.84; N, 14.25. Found: C, 33.09; H, 6.85; N, 14.51.

[Ni(F)](ClO$_4$)$_2$. This compound was prepared by a method similar to that for $[Ni(E)](ClO_4)_2 \cdot H_2O$ except that 98% 2-ethylhexyl amine (8.2 ml) was used instead of *iso*-butylamine. Yield: ~20%. *Anal.* Calcd for $NiC_{24}H_{54}N_6Cl_2O_8$: C, 42.16; H, 7.97; N, 12.29. Found: C, 41.38; H, 8.14; N, 12.54.

[Ni(G)](ClO$_4$)$_2$. This compound was prepared by a method similar to that for $[Ni(E)](ClO_4)_2 \cdot H_2O$ except that 98% benzylamine (5.5 ml) was used instead of *iso*-butylamine. Yield: ~35%. *Anal.* Calcd for $NiC_{22}H_{34}N_6Cl_2O_8$: C, 41.24; H, 5.31; N, 13.12. Found: C, 40.86; H, 5.34; N, 13.10.

[Ni(L)](PF$_6$)$_2$(L = C,D,E,F, or G). To an acetonitrile (20 ml) suspension of ClO_4^- salts of a complex (0.5 g) was added excess NH_4PF_6. The ClO_4^- salts of the complex went into the solution, and precipitates of NH_4ClO_4 were formed. NH_4ClO_4 was removed by filtration, and water (10 ml) was added to the filtrate. The solution was concentrated to ca. 20 ml on a water bath and then cooled. The yellow precipitates formed were filtered, washed with water and methanol, and air-dried.

[Cu(C)](ClO$_4$)$_2$·H$_2$O. To a stirred methanol solution (50 ml) of $CuCl_2 \cdot 2H_2O$ (8.5 g) were added 99% ethylenediamine (6.8 ml), 36% formaldehyde (20.6 ml), and 99% *n*-propylamine (4.2 ml). The mixture was heated at reflux for 24 h and then cooled to room temperature. As excess perchloric acid was added to the mixture, the pale red precipitates formed within a few minutes. The precipitates were filtered, washed with methanol, and air-dried. The product was recrystallized from hot water. Yield: ~25%. *Anal.* Calcd for $CuC_{14}H_{36}N_6Cl_2O_9$: C, 29.66; H, 6.76; N, 14.82. Found: C, 29.28; H, 6.61; N, 15.39.

[Cu(D)](ClO$_4$)$_2$·H$_2$O. This compound was prepared by a method similar to that for $[Cu(C)](ClO_4)_2 \cdot H_2O$ except that 99% *n*-butylamine (10 ml) was employed instead of *n*-propylamine. The red product was recrystallized from a mixture of water-acetonitrile (5:1). Yield: ~25%. *Anal.* Calcd for $CuC_{16}H_{40}N_6Cl_2C_9$: C, 32.27; H, 6.72; N, 14.12. Found: C, 32.84; H, 6.47; N, 13.73.

[Cu(E)](ClO$_4$)$_2$. This compound was prepared by a method similar to that for $[Ni(E)](ClO_4)_2 \cdot H_2O$ by using $CuCl_2 \cdot 2H_2O$ (8.5 g) instead of $NiCl_2 \cdot 6H_2O$. The red precipitates formed rere recrystallized from a mixture of water-acetonitrile (1:1). Yield: ~25%. *Anal.* Calcd for $CuC_{16}H_{38}N_6Cl_2O_8$: C, 33.33; H, 6.64; N, 14.58. Found: C, 32.96; H, 6.64; N, 14.58.

[Cu(F)](ClO$_4$)$_2$. This red compound was prepared by a method similar to that for $[Cu(E)(ClO_4)_2$ except that 98% 2-ethylhexylamine (8.2 ml) was used instead of *iso*-butylamine. Yield: ~20%. *Anal.* Calcd for $CuC_{24}H_{54}N_6Cl_2O_8$: C, 41.85; H, 7.91; N, 12.21. Found: C, 40.75; H, 7.81; N, 12.49.

[Cu(G)](ClO$_4$)$_2$. This compound was prepared by a method similar to that for $[Cu(E)](ClO_4)_2$ except that 98% benzylamine (5.5 ml) was used instead of *iso*-butylamine. Yield: ~35%. *Anal.* Calcd for $CuC_{22}H_{34}N_6Cl_2O_8$: C, 40.93; H, 5.27; N, 13.02. Found: C, 40.70; H, 5.15; N, 13.27.

Results and Discussion

New macrocyclic complexes $[M(L)](ClO_4)_2$(M = Ni(II) or Cu(II); L = C-G) are readily prepared by heating the methanol solutions of ethylenediamine, formaldehyde, and appropriate primary amines in the presence of Ni(II) or Cu(II) chloride, followed by addition of excess perchloric acid or lithium perchlorate. The synthetic routes for the complexes may be similar to those for the complexes of A and B,[5] but the yields are much lower.

All ClO_4^- salts of Ni(II) and Cu(II) complexes of C-G are soluble in polar organic solvents such as MeCN, DMF, $MeNO_2$, or Me_2SO, but insoluble in MeOH or EtOH. The Ni(II) and Cu(II) complexes of C-G except those of F are soluble in water, and the solubility decreases in the order of $A \approx B > C > D > E > G$ as shown in Table 1. This indicates that the solubilities of the complexes are significantly affected by the variation of the pendant arms. The Ni(II) and Cu(II) complexes of C-G are relatively stable against ligand dissociation

Table 1. Solubilities of ClO_4^- Salts of Nickel(II) and Copper(II) Hexaaza Macrocyclic Complexes in Water[a]

ligand	Solubility, mol/*l*	
	Ni(II) complex	Cu(II) complex
A	1.1×10^{-2}	8.6×10^{-3}
B	1.1×10^{-2}	9.1×10^{-3}
C	3.8×10^{-3}	3.7×10^{-3}
D	1.5×10^{-3}	1.2×10^{-3}
E	9.0×10^{-4}	7.9×10^{-4}
F	*i*[b]	*i*
G	4.2×10^{-4}	3.8×10^{-4}

[a] Obtained from electronic spectra of saturated aqueous solutions of complexes at 25 °C. [b] *i* = insoluble.

even in highly acidic solutions. Electronic spectra of aqueous solutions of the complexes (1.0×10^{-3}M) indicate that only 8-20% of the Ni(II) complexes and 1-5% of the Cu(II) complexes were decomposed in 10 h at 25 °C upon the addition of HNO_3(0.3 M).[5,6] Other Ni(II) and Cu(II) complexes of the 14-membered macrocyclic ligands with 5-6-5-6 chelate ring sequence were also reported to decompose slowly even in highly acidic solutions.[18-21]

The infrared and electronic spectra as well as the conductance data of the Ni(II) and Cu(II) complexes are summarized in Tables 2 and 3. The values of molar conductance for the Ni(II) and Cu(II) complexes indicate that the complexes are 1:2 electrolytes. The infrared spectra of the compounds show a N-H stretch for the coordinated secondary amines at ~ 3200 cm^{-1}. The electronic spectra of nitromethane solutions of the Ni(II) complexes show a broad *d-d* transition band near 450 nm (ϵ = 63-79 $M^{-1}cm^{-1}$), and those of the Cu (II) complexes at 485-500 nm (ϵ = 73-87 $M^{-1}cm^{-1}$). The wavelengths and molar extinction coefficients of the bands are comparable to the values reported for other square planar Ni(II) and Cu(II) complexes with A, B, or other 14-membered macrocycles.[5,22-28] Moreover, the spectra indicate that the ligand field strength of the complexes are not affected by the variation of the alkyl groups at the uncoordinated nitrogen atoms. The spectra of nickel(II) complexes measured in

Table 2. Spectral and Conductance Data of Nickel(II) Macrocyclic Complexes

Complex	IR, cm^{-1}	Electronic spectra λ_{max}, nm(ϵ, $M^{-1}cm^{-1}$)			Λ_M[b], $ohm^{-1}mol^{-1}cm^2$	Ref.
		CH_3CN	CH_3NO_2	H_2O		
$[Ni(A)](ClO_4)_2$	ν_{NH} 3220	460(32)	449(56)	446(40)		5
$[Ni(B)](ClO_4)_2$	ν_{NH} 3185	461(35)	449(64)	445(47)		5
$[Ni(C)](ClO_4)_2$	ν_{NH} 3190	450(33)	448(65)	442(59)	278, 210[c]	this work
$[Ni(D)](ClO_4)_2$	ν_{NH} 3190	452(39)	446(74)	444(50)	254	this work
$[Ni(E)](ClO_4)_2$	ν_{NH} 3190	453(32)	446(62)	443(52)	286	this work
$[Ni(F)](ClO_4)_2$	ν_{NH} 3200	450(46)	447(79)		280	this work
$[Ni(G)](ClO_4)_2$	ν_{NH} 3180, ν_{CH} 3050[a] $\nu_{C=C}$ 1600, 1580[a]	450(34)	447(69)	446(54)	250	this work
$[Ni([14]aneN_4)]^{2+}$[d]				460(68)		22
$[Ni(Me_2[14]aneN_4)]^{2+}$[e]				441(62)		23
$[Ni(Me_6[14]aneN_4)]^{2+}$[f]				443(70)		24

[a] Peaks of phenyl rings. [b] In acetonitrile solutions at 25 °C unless otherwise specified. [c] In aqueous solution at 25 °C. [d] $[14]aneN_4$ = 1,4,8,11-tetraazacyclotetradecane. [e] $Me_2[14]aneN_4$ = 5,7-dimethyl-1,4,8,11-tetraazacyclotetradecane. [f] $Me_6[14]aneN_4$ = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane.

Table 3. Spectral and Conductance Data of Copper(II) Macrocyclic Complexes

Complex	IR, cm^{-1}	Electronic spectra λ_{max}, nm(ϵ, $M^{-1}cm^{-1}$)			Λ_M[b], $ohm^{-1}mol^{-1}cm^2$	Ref.
		CH_3CN	CH_3NO_2	H_2O		
$[Cu(A)](ClO_4)_2$	ν_{NH} 3232	498(76)	486(73)	500(80)		5
$[Cu(B)](ClO_4)_2$	ν_{NH} 3232	495(81)	485(77)	501(84)		5
$[Cu(C)](ClO_4)_2$	ν_{NH} 3240	505(85)	489(87)	498(83)	285, 215[c]	this work
$[Cu(D)](ClO_4)_2$	ν_{NH} 3235	495(85)	484(80)	495(87)	285	this work
$[Cu(E)](ClO_4)_2$	ν_{NH} 3240	493(83)	482(82)	494(85)	287	this work
$[Cu(F)](ClO_4)_2$	ν_{NH} 3230	493(90)	485(87)		290	this work
$[Cu(G)](ClO_4)_2$	ν_{NH} 3230, ν_{CH} 3050[a] $\nu_{C=C}$ 1600, 1580[a]	504(90)	491(84)	502(89)	271	this work
$[Cu([14]aneN_4)]^{2+}$[d]				508(92)		28
$[Cu(Me_2[14]aneN_4a)]^{2+}$[e]				610(85)		27

[a] Peaks of phenyl rings. [b] In acetonitrile solutions at 25 °C unless otherwise specified. [c] In aqueous solution at 25 °C. [d] $[14]aneN_4$ = 1,4,8,11-tetraazacyclotetradecane. [e] $Me_2[14]aneN_4$ = 5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane.

Table 4. ^{13}C-NMR Spectral Data of the Nickel(II) Hexaaza Macrocyclic Complexes[a]

ligand	δ, ppm					
	N-C-N	N-C-C-N	substituent(R)			
A[b]	70.0	48.6	38.3			
B[b]	68.7	48.5	48.6	13.3		
C	69.1	48.5	52.5	22.5	11.5	
D	69.1	48.2	50.5	30.9	20.7	14.0
E	69.4	48.3	58.8	28.1	20.1	
F	69.4	48.3	54.3	38.4	31.0	29.4
			24.3	24.0	14.4	10.6
G	69.2	48.6	55.3	130.0	129.6	129.2

[a]Measured in CD_3NO_2 solutions. [b]Reference 5.

Table 5. Cyclic Voltammetric Data for Nickel(II) and Copper(II) Macrocyclic Complexes[a,b]

complex	$[M(L)]^{2+} \rightarrow [M(L)]^{3+}$	$[M(L)]^{2+} \rightarrow [M(L)]^{+}$	ref.
Ni(A)	+0.93	-1.54	5
Ni(B)	+0.92	-1.47	5
Ni(C)	+0.94	-1.54	this work
Ni(D)	+0.94	-1.55	this work
Ni(E)	+0.95	-1.52	this work
Ni(F)	+0.95	-1.49	this work
Ni(G)	+0.97	-1.51	this work
Ni([14]aneN$_4$)	+0.91	-1.46	34
Ni(Me$_2$[14]aneN$_4$)	+0.92	-1.49	34
Cu(A)	+1.32	-1.14(*i*)	5
Cu(B)	+1.35	-1.07(*i*)	5
Cu(C)	+1.31	-1.09(*i*)	this work
Cu(D)	+1.31	-0.98(*i*)	this work
Cu(E)	+1.31	-1.16(*i*)	this work
Cu(F)	+1.33	-1.18(*i*)	this work
Cu(G)	+1.33	-1.15(*i*)	this work
Cu([14]aneN$_4$)	+1.34	-1.10	35

[a]Measured in 0.1 M (n-Bu)$_4$NClO$_4$ acetonitrile solutions; Volts *vs.* SCE. [b]*i* = irreversible.

acetonitrile or water show much lower extinction coefficients than those measured in nitromethane solutions as shown in Table 2. This indicates that the Ni(II) complexes exist in acetonitrile or water solutions as equilibrium mixtures of square planar $[Ni(L)]^{2+}$ and octahedral $[Ni(L)(S)_2]^{2+}$ (S = solvent) species. This equilibrium has been observed for other Ni(II) complexes also.[5,29-33] ^{13}C-NMR spectra of PF_6^- salts of Ni(II) complexes are measured in CD_3NO_2 solutions and are summarized in Table 4, which are consistent with the ligand structures of C-G. The carbon peaks of N-C-N and N-C-C-N linkages of the macrocyclic ligands are observed near 69 ppm and 48 ppm, respectively. Cyclic voltammetry data for the Ni(II) and Cu(II) complexes are represented in Table 5. All Ni(II) and Cu(II) complexes show an one-electron oxidation and an one-electron reduction waves corresponding to M(II)→ M(III) and M(II)→ M(I) processes. The oxidation and the reduction potentials of Ni(II) and Cu(II) complexes with C-G are comparable to the values for the complexes of A, B, [14]aneN$_4$, and other 14-membered tetraaza macrocyclic ligands.[5,34-37] Furthermore, the oxidation and reduction potentials do not vary considerably as different alkyl group are attached to the uncoordinated nitrogen atoms in the hexaaza macrocyclic complexes. That is, the electron density on the metal atom or hole size of the macrocycles in the complexes is not affected significantly by the nature of the alkyl pendant arms.

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Novel Synthesis of C-3 Vinylic Cephem Systems

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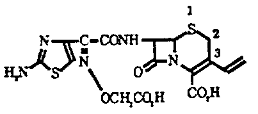
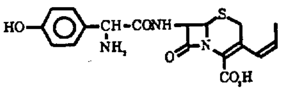
The 3-formyl-2-cephem **4**, available from 7-aminocephalosporanic acid has been converted to C-3 vinylic cephems. The reactions involved are the Grignard addition to **4**, the conversion of the resulting alcohols to mesylates, and the elimination of the mesyl group by LiCl. When ethylmagnesium iodide is used, only 3-[(E)-1-propenyl] cephem is obtained, which is not easily available by conventional Wittig reaction.

Introduction

Cefixime is the first cephalosporin antibiotic having a vinyl group at C-3 position, which was developed by Fujisawa company as an orally administrable drug in 1983.[2] Since then, the syntheses of cefixime analogs have been reported in the literature. For example, Bristol-Myers company reported the preparation of (Z)-1-propenyl derivative named BMY-28100.[3]

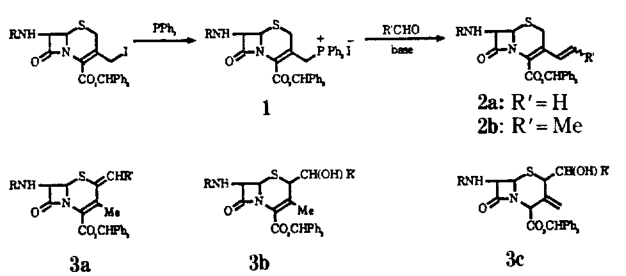


Cefixime



BMY-2810

Literature preparations of cefixime and BMY-28100 involve a Wittig-type reaction, namely a coupling of cephem-derived triphenylphosphonium salt **1** with formaldehyde and acetaldehyde in the presence of base, respectively, as shown in Scheme 1.[2,3]



Scheme 1

In the Wittig reaction with acetaldehyde, the major (Z)-product **2b** is contaminated with ca. 15-20% of the minor (E)-isomer. The separation of this two isomers requires the tedious preparative HPLC method.

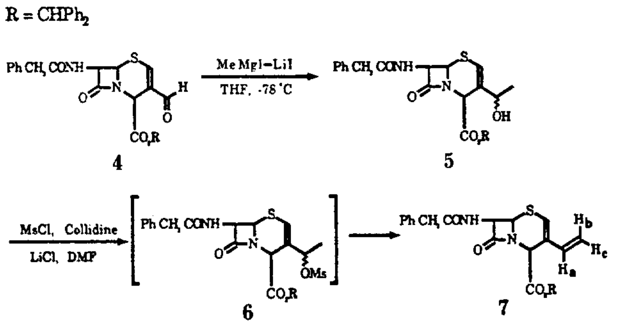
Also, it is generally known that the cephem ylide is less reactive to higher aliphatic aldehydes than to formaldehyde, giving various C-2 substituted compounds **3a** to **3c** as well as the expected Wittig product.[4]

We thought that 3-formyl-2-cephem **4** (Scheme 2), easily available starting from 7-aminocephalosporanic acid could serve as a useful starting material for the preparation of 3-vinylic cephem system.[5]

We wish to report a transformation of **4** to 3-vinylic cephem in 2-cephem system.

Result and Discussion

When 3-formyl-2-cephem **4** was treated with a large ex-



Scheme 2