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New Cryptand Complexes of Lanthanides(III) and Dioxouranium(VI) Nitrates

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The following new cryptand 221 complexes of lanthanides(III) and dioxouranium(VI) nitrate have been synthesized: $(Ln(C_{16}H_{32}N_2O_5)(H_2O)_2(NO_3)_3)$ and $((UO_2)_2(C_{16}H_{32}N_2O_5)(H_2O)_4)(NO_3)_4$. These complexes have been identified by elemental analysis, moisture titration, conductivity measurements and various spectroscopic techniques. The proton and carbon-13 NMR as well as calorimetric measurements were used to study the interaction of cryptand 221 with La(III), Pr(III), Ho(III) and $UO_2(II)$ ions in nonaqueous solvents. The bands of metal-oxygen atoms, metal-nitrogen atoms and O-U-O in the IR spectra shift upon complexation to lower frequencies, and the vibrational spectra (δ NMN) of metal-amide complexes in the crystalline state exhibit lattice vibrations below 300 cm^{-1} . The NMR spectra of the lanthanides(III) and dioxouranium(VI) nitrate complexes in nonaqueous solvents are quite different, indicating that the ligand exists in different conformation, and also the 1H and ^{13}C -NMR studies indicated that the nitrogen atom of the ring has greater affinity to metal ions than does the oxygen atom, and the planalities of the ring are lost by complexation with metal ions. Calorimetric measurements show that cryptand 221 forms more stable complexes with La^{3+} and Pr^{3+} ions than with UO_2^{2+} ion, and La^{3+}/Pr^{3+} and UO_2^{2+}/Pr^{3+} selectivity depends on the solvents. These changes on the stabilities are dependent on the basicity of the ligand and the size of the metal ions. The absorption band (230-260 nm) of the complex which arises from the direct interaction of macrocyclic donor atoms with the metal ion is due to $n\text{-}\delta^*$ transition and also that (640-675 nm) of UO_2^{2+} -cryptand 221 complex, which arises from interaction between two-dioxouranium(VI) ions in being out of cavity of the ligand ring is due to $d\text{-}d^*$ transition.

Introduction

Since the discovery of the metal-template synthesis by Curtis¹ and Buson² thirty years ago, the field of macrocyclic ligands has become a major area of research. The chemistry of first-row transition-metal ions complexed by macrocyclic ligands has been extensively developed and exhibits many unusual features compared to noncyclic analogues.

The macrocycles have been shown to stabilize high oxidation states of metal ions such as $Ag(II)^3$ and $Ni(III)^4$. They exhibit unusual ligand field strengths compared to noncyclic ligands with similar donor atoms⁵, and the formation constants of their metal complexes are often unusually high.

One of the fundamental properties of these ligands is the size of the macrocyclic ring. A change in ring size on high spin⁶ and on low spin⁷ complexes has been shown to affect

the electronic spectra, redox potentials and reactivity of complexes markedly. Many communications on the synthesis and structural characteristics of the dioxouranium(VI) and lanthanide(III) complexes with crown ether and crownand macrocyclic ligands have been published^{8, 23, 26}, as have communications on the synthesis and structural characteristics of some lanthanide complexes with cryptand 222 (Cryptand 222 = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-(8,8,8)hexacosane) using various spectroscopic and X-ray crystal studies¹¹. As an extension of our previous studies on the synthesis, structure and electronic properties of lanthanoid(III) and dioxouranium(VI) complexes⁹, we are now interested in a systematic investigation of coordination compounds of these metal ions with macrocyclic ligands of cryptand 221.

The cryptand 221(4,7,13,16,21-pentaoxa-1,10-diazabicyclo-(8,8,5)tricosan) ligand is fully saturated in donor electrons of

two-nitrogen and five-oxygen atoms, which have the δ -donors only, and its electronic spectra will not show complications from π -bonding. This ligand forms remarkably stable complexes with some alkali metal ions²⁰, but any experimental results on the dioxouranium(VI) and lanthanoid(III) complexes with this ligand have not been reported previously. In an effort to extend such studies to lanthanides(III) and dioxouranium(VI) metal ions, we undertook the synthesis and structural characterization of a series of lanthanoids(III) and dioxouranium(VI) complexes. The observation of several spectroscopic properties of these complex systems reported herein allows for the characterization of such behavior. All of spectroscopic measurements have been used to provide structural information. Additionally, the affinity of donor atoms to metal ions and changes in the planarity of the macrocyclic ring upon complexation with metal ions have been observed, and also the selectivity and stability of each complex have been investigated using ¹³C-NMR spectroscopy and solution calorimetry.

Experimental

Reagent. Cryptand 221 (Merck) was dried in a vacuum at 25°C for 2 days. Solvents used for the study were purified by the techniques described below; acetone (Sigma), acetonitrile (Aldrich) and methanol (Wako) were refluxed over calcium hydroxide for 12-24 hr and then fractionally distilled.

The water content of the solvents was checked by automatic Karl Fischer titration with a Tokyo Electronics and was always below 100 ppm. The purity of the solvents was also checked by ¹³C-NMR, and no detectable amount of impurities were found.

The deuterated solvents, acetonitrile-d₃ (Aldrich, Gold Label), dimethylsulfoxide-d₆ (Aldrich, Gold Label), chloroform-d (Aldrich, Gold Label) and D₂O (SIC) were used as NMR solvents. Lanthanum(III), praseodymium(III), holmium(III) and dioxouranium(VI) nitrate hydrates (Sigma, GR) were dried for 24 hr.

Complexes. All of the complexes were prepared according to the methods of Poon¹⁰ and Seminar¹¹. A solution of 2.0 mmol ligand in 30 ml-solvents (methanol, acetonitrile and acetone) was added dropwise to a solution of 3.0-4.5 mmol metal salt in 20 ml solvents under nitrogen atmosphere, and the mixture was stirred at 30°C for 12 hr.

The polycrystalline complex was filtered, washed with 30 ml CH₂Cl₂, dried in a deccicator over P₂O₅ for 2 days, and dried under a vacuum (10⁻² Torr) for 3-10 days, yielding 80-92% for each complex.

The data of elemental analysis and hydrate titration of each

complex were obtained by a Yamato C H N coder MT-3, Labtest 710 ICPAC and Kyoto electronic model MK-20 Karl Fisher moisture titrator. The quantity of NO₃⁻ in each complex was determined by an Orion 960 auto chemistry system equipped with a NO₃⁻ ion selective electrode, and the molar conductivities¹² of the complexes were measured with a Kyoto electric CM-07 digital conductivity bridge.

Calorimetric Measurements. The concentration of cryptand 221 was 5.0 × 10⁻³ M and the concentration of metal salts were 5.0 × 10⁻³ M. The same batch of purified solvent was used for the preparation of the complexes.

The heats of complexation were measured at 25 ± 0.1°C with a Tronac model 87-458 microcalorimeter equipped with a recorder and a curve integrator.

The flow of the salt solutions was 2.5 times faster than the flow of the ligand solution. The quantity of the ligand consumed was derived from the determination of the flow rate and the injection time of the ligand solution. The base line was fixed by the mixing of the salt solution with the pure solvents.

The heat of dilution of the ligand was considered to be negligible. The measurements were repeated at least three times and the reproducibility of the ΔH values was ± 0.1 kcal mol⁻¹.

Proton NMR Measurements. Proton NMR measurements were carried out on a Bruker FT-300 MHz spectrometer. The chemical shifts were referenced to Me₄Si.

Carbon-13 Measurements. Carbon-13 measurements were carried out on a Bruker FT-300 MHz spectrometer. The sample solutions were placed in a 5 mm. o.d. NMR tube which was coaxially inserted in a 10 mm. o.d. NMR tube containing dimethylsulfoxide-d₆ as the lock. The methyl carbon peak of dimethylsulfoxide-d₆ was used as the external reference. The chemical shifts were corrected for the differences in bulk magnetic susceptibilities between the sample solvent and acetonitrile.

Selectivity Measurements. The UO₂²⁺/Ln³⁺ and La³⁺/Pr³⁺ selectivity measurements were carried out with ¹³C-NMR. Since the species UO₂²⁺-cryptand 221 and Ln³⁺-cryptand 221 are in slow exchange in solvents such as methanol, acetonitrile and acetone, the concentrations of each complex ion were determined by integrating the ¹³C resonance lines. The concentration of the free metal ions obtained from the known total concentration of the salts and of the cryptands.

Spectroscopic Spectra. Electronic spectra of each complex were obtained from a solution of methanol, water and dimethylformamide on a Hitachi Model U-3140 double beam UV/Vis spectrophotometer, and the IR-spectra were obtained from KBr pellets on a Perkin-Elmer 1310 FTIR

Table 1. Analytical Data and Conductivity of Dioxouranium(VI) and Lanthanide(III) Complexes with Cryptand 221

Complexes	Calc.(%)					Found(%)					Molar Conductance (cm ² ·mol ⁻¹ ·ohm ⁻¹)	
	C	H	N	metal	H ₂ O	C	H	N	metal	H ₂ O	H ₂ O	DMF
(UO ₂) ₂ [C ₁₆ H ₃₂ N ₂ O ₅ (H ₂ O) ₄](NO ₃) ₄	16.8	3.52	7.34	41.6	6.30	16.1	3.58	7.28	40.8	6.34	268	301
La[(C ₁₆ H ₃₂ N ₂ O ₅ (H ₂ O) ₂](NO ₃) ₃	27.7	5.23	10.1	20.0	5.20	27.8	5.25	10.3	20.2	5.26	394	432
Pr[(C ₁₆ H ₃₂ N ₂ O ₅ (H ₂ O) ₂](NO ₃) ₃	27.4	5.17	9.97	21.1	5.13	27.3	5.16	10.1	21.8	5.16	392	426
HO[(C ₁₆ H ₃₂ N ₂ O ₅ (H ₂ O) ₂](NO ₃) ₂	26.7	5.04	9.74	22.9	5.01	26.8	5.10	9.82	22.7	5.14	382	418

spectrophotometer.

Results and Discussion

Results of the elemental analyses and contents of hydrates in each complex are shown in Table 1.

All of the complexes of lanthanides(III) with cryptand 221 ligand are hygroscopic and form dihydrates, whereas the complex of dioxouranium(VI) is not hygroscopic and forms tetrahydrates.

All of the complexes of lanthanides(III) have 1:1 stoichiometry and are soluble in protic and aprotic solvents, but the complex of dioxouranium(VI) has 1:2 stoichiometry for cryptand 221 to dioxouranium(VI) metal and is soluble in the same solvents.

Since the cryptand 221 ligand has relatively strong basic properties, the synthesis of the lanthanides(III) and dioxouranium(VI) cryptates starting from hydrated cations are strongly hampered by the formation of hydroxo compounds and N-protonated species.

The conductivity of the lanthanides(III) and dioxouranium(VI) nitrates in acetonitrile and water increases, and the molar conductivity for the complexes of the cryptand 221 molecules with lanthanide(III) nitrates in dimethylformamide and water solvents is in the range of 394 to 432 $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$ and also those with dioxouranium(II) nitrate in the same solvents is in the range of 268 to 301 $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$ for $1-1.5 \times 10^{-3} \text{ M}$ concentration at 25°C.

The conductivity measurements were performed also by addition of known amounts of the cryptand 221 and the cation in acetonitrile. The conductivity became constant and reached the value measured for the corresponding complex dissolved in the same solvent after the addition of 1 mmol of cryptand 221 and 1-2 mmol of the cations.

The results of plot for equivalent conductivity vs concentration of ligand give a distinct break at $C_M/C_L=1:1$ for the systems of rare earth metal ions-cryptand 221, indicating that only a 1:1 complex is formed. Whereas, the slope of curve for the system UO_2^{2+} -cryptand 221 change sharply near the point $C_M/C_L=2:1$, indicating the cryptand 221 forms complex with UO_2^{2+} stoichiometrically. And it shows that the complexes of lanthanides(III) nitrate have been dissociated as 1:3 and the complex of dioxouranium(VI) nitrate has been dissociated as 1:2 electrolytes¹² in water and acetonitrile solvent, respectively. Therefore, the composing formulas of lanthanides(III) and dioxouranium(VI) nitrate complexes with cryptand 221 are $(\text{Ln}(\text{C}_{16}\text{H}_{32}\text{N}_2\text{O}_5)(\text{H}_2\text{O})_2)(\text{NO}_3)_3$ and $(\text{UO}_2)_2(\text{C}_{16}\text{H}_{32}\text{N}_2\text{O}_5)(\text{H}_2\text{O})_4(\text{NO}_3)_4$ respectively.

IR Spectra. The IR bands exhibited by these molecules which undergo significant changes on complexation with metal ions are those arising from C-O-C and C-N-C stretching and CH bending modes (Figure 1).

The C-O-C and C-N-C stretching modes, which show strong and broad bands around $1220-1130 \text{ cm}^{-1}$ in the spectra of the free ligands, shift upon complexation $40-90 \text{ cm}^{-1}$ to lower frequencies. The CH bending modes which appear at $950-940 \text{ cm}^{-1}$ in the spectra of the ligands shift $15-40 \text{ cm}^{-1}$ to higher frequencies. These spectral changes are similar to those reported for the lanthanide(III) nitrate complexes with tetraoxadiazacrown ethers and other cryptand macrocyclic molecules^{13,14}. In general, lattice water absorbs at $3550-$

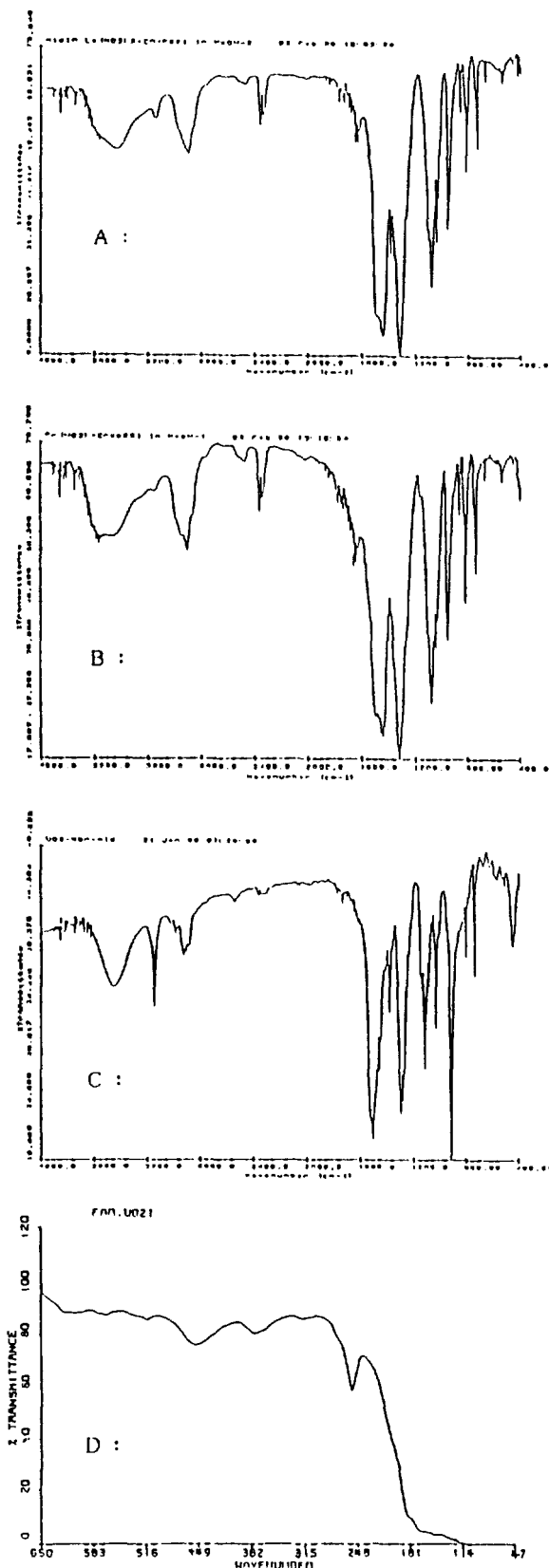


Figure 1. IR-Spectra of lanthanides(III) and dioxouranium(VI) nitrate complexes with cryptand 221. A: mid-IR-spectrum of La(III) complex, B: mid-IR-spectrum of Pr(III) complex, C: mid-IR-spectrum of dioxouranium(VI) complex and D: far-IR-spectrum of dioxouranium(VI) complex.

Table 2. Infrared Data(cm^{-1}) for Ligand and Its Complexes

Bonds	Assignment (cm^{-1})			
	Ligand or metallic nitrate	Complexes		
		UO_2^{2+}	La^{3+}	Pr^{3+}
R-O-CH ₂	1056(s), 2880(s)	1045(s)	1048(m)	1024(m)
-N=	2960(s), 2760(s)	2920(s)	2896(m)	2893(m)
	1450(m), 1220(m)	2700(s)	2792(w)	2752(w)
		1390(s)	1376(m)	1376(m)
C-O-C	1130(s)	1180(m)	1152(m)	1144(w)
UO_2^{2+}	930(s)	1080(s)	1104(s)	1074(s)
OH ₂	3440(U-lattice, s), 1620 (U-lattice, w)	3340(m)	3420-3260(m)	3428-3280(m)
	3500-3250(Ln-lattice, s)			
	1616(Ln-lattice, s)			
M-OH ₂	-- -- -- --	452(m)	465(w)	468(w)
M-O	-- -- -- --	621(w)	653(w)	657
		576	556	558
		516	428	429
		367,312	351,335	348,337
M-N	-- -- -- --	1024(m)	1048(m)	1024(m)
		736(m)	744(m)	745(w)
		252(m)	294(w)	290(w)
NO ₃ ⁻	$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; 1530(ν_1) 1352(ν_3) 1040(ν_2) 810(ν_6) 720(ν_5/ν_3) 1480 1330(ν_4) 1020 1454	1472(ν_1) 1346(ν_3) 1038(ν_2) 810(ν_6) 695(ν_5/ν_3)	--	--
	$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$; 1568(ν_1) 1348(ν_4) 1120(ν_2) 800(ν_6) 752(ν_5/ν_3) 1444 1104	--	1492(ν_1) 1346(ν_3) 1120(ν_2) 1432 848(ν_6) 738(ν_5/ν_3)	1504(ν_1) 1320(ν_3) 1088(ν_2) 800(ν_6) 725(ν_5/ν_3) 1456(ν_1)

3200 cm^{-1} and at $1630\text{-}1600 \text{ cm}^{-1}$ but the spectra of hydrated water molecules in these complexes appear at lower frequencies with respect to the lattice water (Table 2).

This suggests that true coordination of water molecules does not occur in these cases but interaction of the outersphere type only or hydrogen bonds acts between the cryptand and water molecules of adjacent entities^{15,16}.

Only bands arising from the nitrate group of C_{2v} symmetry appear in the IR spectra of the nitrate complexes with cryptand 221, and the appearance of a band at $1346\text{-}1320 \text{ cm}^{-1}$ due to the ν_3 mode suggests ionization of nitrate groups. However, splitting occurs for the ν_2 , ν_3 and ν_6 modes. The spectral patterns are shown in the data of Table 2. The metal-to-oxygen bands from donating atoms of cryptand 221 ligand are exhibited at far-IR range¹⁷, which is illustrated in Figure 1 and Table 2, and also metal-to-oxygen bands from donating atoms of hydrates are exhibited at $452\text{-}465 \text{ cm}^{-1}$ respectively. The metal to nitrogen bands which appear upon complexation at 1048 , 1024 , 736 and 745 cm^{-1} in the spectra are exhibited at higher frequencies than metal-oxygen bands. These spectra changes are similar to those reported for the other complexes with noncyclic ligands^{18,19}, and the band of red shift which appears at 294 , 290 and 252

cm^{-1} is considered to be diagnostic of amide coordination to a Lewis acid through the nitrogen atom in the ligand. Finally, the $\text{O}=\text{U}=\text{O}$ stretching mode which appears as a strong and sharp band at 930 cm^{-1} in the spectra of the $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ shifts upon complexation 35 cm^{-1} to lower frequency.

Proton NMR Spectra. Several representative $^1\text{H-NMR}$ spectra of the title compounds are shown in Figure 2, and the signal assignments of these spectra have been verified by decoupling methods. In complexes of lanthanides(III), the geminal methylene proton to bridgehead nitrogens on the two oxygen strands seems to exhibit an AM doublet with $J_{MX}=13.7 \text{ Hz}$, which is vicinally coupled to the adjacent β -CH₂ group denoted as protons H_x and H_y with $J_{AX}=J_{AY}=3.36$, $J_{MY}=5.49$ and $J_{MX}=9.00 \text{ Hz}$, respectively⁹. Therefore the hydrogen atoms bound to nitrogen belonging to the N_2O_4 face form an AMXY system with the neighboring O-CH₂, whereas the $\text{NCH}_2\text{CH}_2\text{O}$ protons of the short chain form an AA'XX' system. In this spectral region the main difference between the spectra of the La^{3+} and Pr^{3+} -complex is the value of the diastereotopy (0.232 ppm for La^{3+} -cryptand 221 and 0.286 ppm) for Pr^{3+} cryptand 221 as H_k proton in Figure 2. These spectral changes are similar to those reported for the alka-

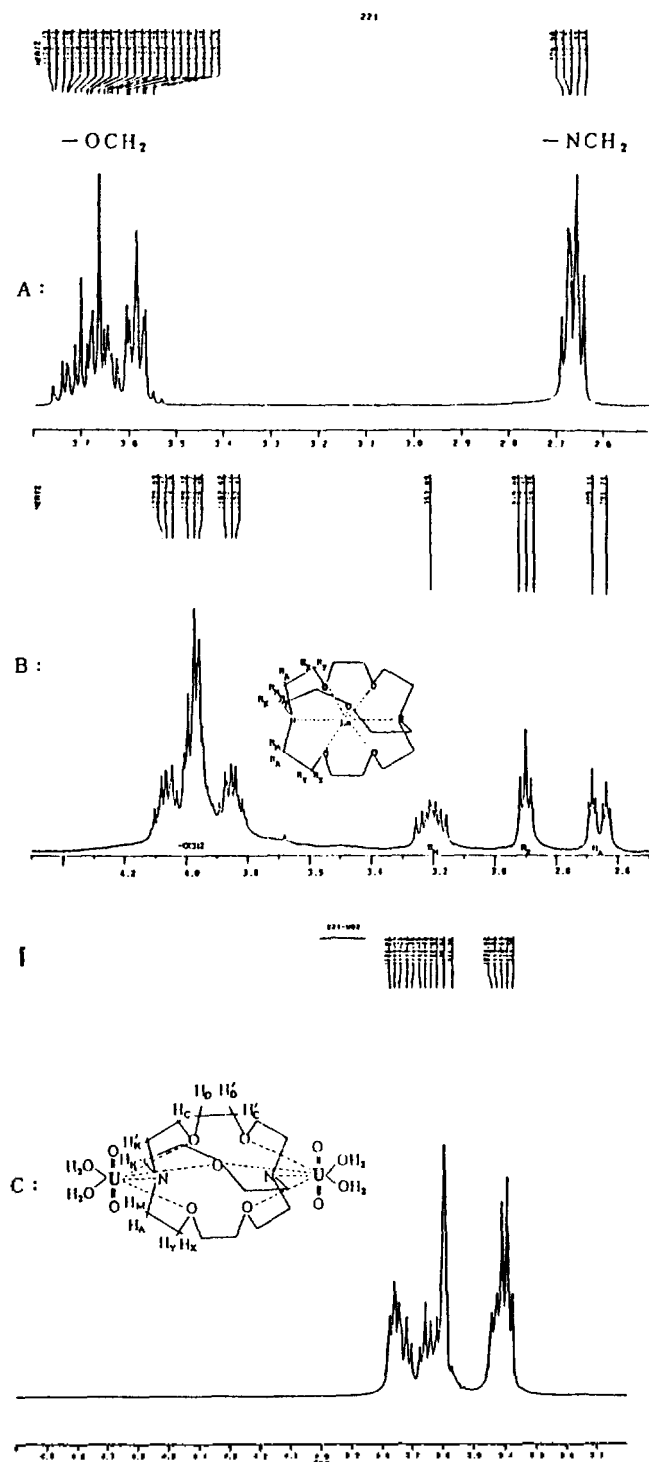


Figure 2. $^1\text{H-NMR}$ spectra of cryptand 221 and its complexes. A: Cryptand 221, B: La(III) complex and C: $\text{UO}_2(\text{II})$ complex.

line metal complexes with cryptand 221²⁰.

In the $^1\text{H-NMR}$ spectrum of UO_2^{2+} -cryptand 221 complex, the geminal methylene protons of the O-CH_2 group, denoted as protons H_C , H_D , $\text{H}_{D'}$ and $\text{H}_{C'}$ are represented by the four triplet patterns because the degree of hindered rotation for the nitrogen-bounded hydrogen atoms belonging to the N_2O face is decreased, but that for the hydrogen atoms β to oxygen belong to the same face is increased by coordinat-

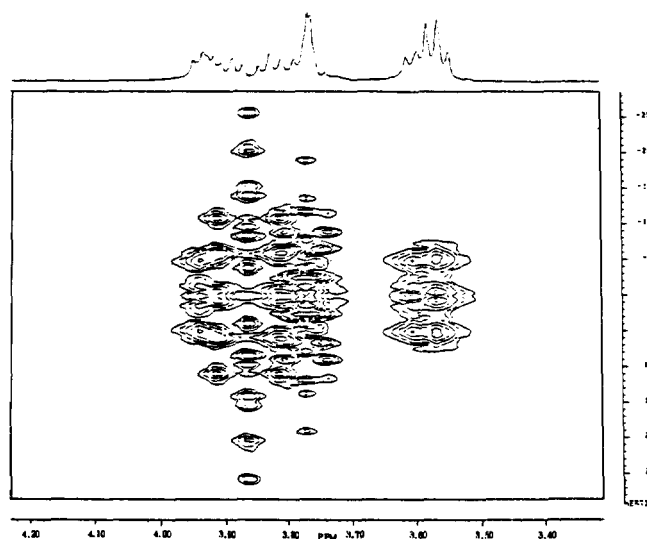


Figure 3. ^1H J-Resolved NMR spectrum of dioxouranium(VI) complex with cryptand 221.

with UO_2^{2+} (Figure 3). The strong and broad band which is exhibited at 3.60 ppm in proton NMR spectra as a result of the methylene protons of ligand was mixed with protons of hydrates coordinated through the oxygen atoms of water molecules. These results are in accord with the analytical data of moisture-titration and IR spectra. The A and B branches of the $\text{AA}'\text{BB}'$ system due to protons H_C , H_D , $\text{H}_{D'}$ and $\text{H}_{C'}$ ($J_{CD}=33.5$ Hz) may be seen on either side of complex patterns which are made up of the triplet of the CH_2 protons of the dioxygen strands, but $^1\text{H-NMR}$ patterns of the geminal methylene protons to bridgehead nitrogen on the oxygen strands are to that of the ligand. This trend is a clear indication of occurrence of the coupling of only O-CH_2 protons in the UO_2^{2+} -cryptand 221 complex.

$^{13}\text{C-NMR}$ Spectra. The cryptand 221 ligand has five different carbon-13 resonances, and resonances of the free ligand, UO_2^{2+} , La^{3+} and Pr^{3+} complexes in deuteriodimethylsulfoxide solutions are shown in Figure 4. The assignments are given according to the numbering of carbon atoms in Figure 4. Assignments are obvious for carbons 3, 4 and 5, but carbons 1 and 2 are assigned by measuring the satellite $^{13}\text{C-}^{13}\text{C}$ coupling patterns with the INADEQUATE pulse sequence²¹. In the satellite spectrum, carbons 2 and 4 form an AX system with $J=45$ Hz, whereas no satellite spectrum is obtained for carbon 1. It is immediately obvious not only that the complexation results in substantial modification of the spectrum obtained in the ligand, but also that the spectra of the three cryptates are very different. These trends are similar to those reported for the other complexes with cryptand 221²⁰.

The results of Figure 4 have been summarized in Table 4, and Figure 4. Table 3 show that carbon-resonances of La^{3+} -cryptand 221 are all upfield from those of the Pr^{3+} -cryptand 221 complex, and also carbon-resonances of $(\text{UO}_2^{2+})_2$ -cryptand 221 are all upfield from those of the Ln^{3+} -cryptand 221 complexes. All of the carbons of $(\text{UO}_2)_2$ -cryptand 221 become more separated than the carbons of the Ln^{3+} -cryptand 221 complexes, and $(\text{UO}_2)_2$ -cryptand resonances are up-

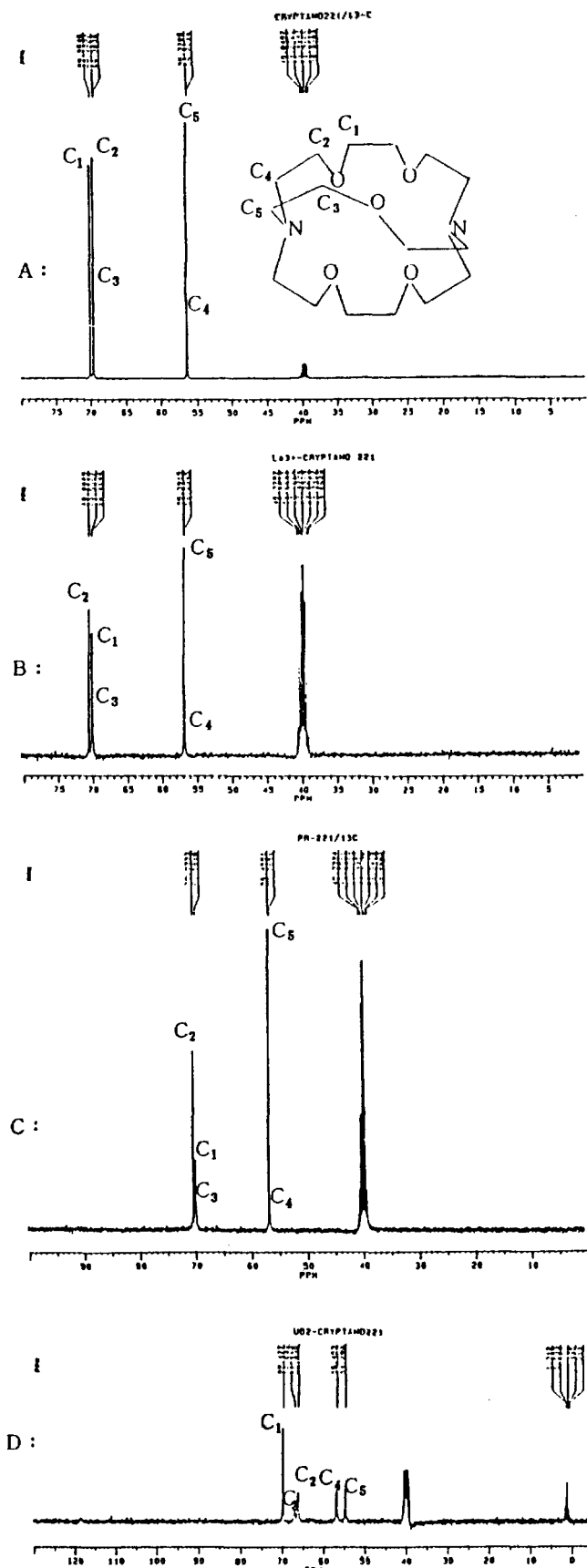


Figure 4. ^{13}C -NMR spectra of cryptand 221 and its complexes. A: cryptand 221, B: La(III) complex, C: Pr(III) complex, and D: $\text{UO}_2(\text{II})$ complex.

Table 3. The ^{13}C Chemical Shift of UO_2^{2+} and Rare Earth Metal Ion Complexes with Cryptand 221

Complexes	Resonance lines(ppm)				
	C ₁	C ₂	C ₃	C ₄	C ₅
Ligand	69.71	69.48	69.36	56.38	56.22
UO_2^{2+}	69.48	66.69	65.38	56.45	54.29
	(+0.488)	(+2.79)	(+3.54)	(-0.076)	(+1.93)
La^{3+}	69.99	69.54	69.41	56.39	56.24
	(-0.023)	(-0.054)	(-0.051)	(+0.013)	(-0.013)
Pr^{3+}	70.02	69.58	69.48	56.46	56.27
	(-0.077)	(-0.097)	(-0.120)	(+0.080)	(-0.044)

Table 4. Selective Coefficients for the Complexation of UO_2^{2+} , La^{3+} , and Pr^{3+} Ions with Cryptand 221 at 25°C

Solvent	ratio of selective coefficient	
	$K_{\text{La}^{3+}}/K_{\text{Pr}^{3+}}$	$K_{\text{La}^{3+}}/K_{\text{UO}_2^{2+}}$
CH_3COCH_3	21.3	25.2
CH_3OH	16.8	21.5
CH_3CN	0.73	0.86

filed from those of the cryptand 221 ligand except the carbon 5, whereas Ln^{3+} -cryptand 221 resonances are downfield from those of the same ligand except carbon 5.

These differences very probably reflect the different structures of the three cryptates in solution. In case of the Lanthanide(III) cryptates, the cation(Ln^{3+}) are in the center of the ligand cavity, and it seems that N-N distance of Pr^{3+} -cryptand 221 complex becomes more decreased than that of La^{3+} -cryptate by the complexation with metal ions because the size of the Pr^{3+} ion is smaller than that of the La^{3+} ion. By contrast, UO_2^{2+} cation is located out of the cavity of the 18-membered ring (2.68-2.86 Å) of the ligand because of the steric hindrance of UO_2^{2+} . Several torsion angles in the La^{3+} -cryptand 221, Pr^{3+} -cryptand 221 and UO_2^{2+} -cryptand 221 complexes are different, but the decrease in cavity size of the complexes is mainly due to change in torsion angles for one O-C₂ (Table 3).

The overall upfield shift of the ^{13}C resonance lines in the La^{3+} -cryptand 221 complex compared to Pr^{3+} -cryptand 221 must be due to an increase of interaction in the C₄-C₂-O-C₁ or C₂-C₄-N-C₅ fragments. From the large separation of carbon 4 and 5 resonance lines for Pr^{3+} cryptand 221 (δ_4 - δ_5 =0.124), as compared with that of La^{3+} -cryptand 221 (δ_4 - δ_5 =0.026), it would be expected that the two complexes also have different structures in solution and that these differences will be reflected in the distortion of the complexed ligand²⁰.

If the types of complexed ligand have the distorted structure, the electronegativity of atoms in macrocyclic ligand is increased due to the effect of anions (NO_3^-) around the complexed cation. This trend shows that ^{13}C -resonance lines are upfield from those of free ligand²². ^1H and ^{13}C -NMR studies indicate that the nitrogen and oxygen atoms of the ring have an affinity to metal ions, and the planarity of the ring is lost by the complexation with metal ions. The ratios of selec-

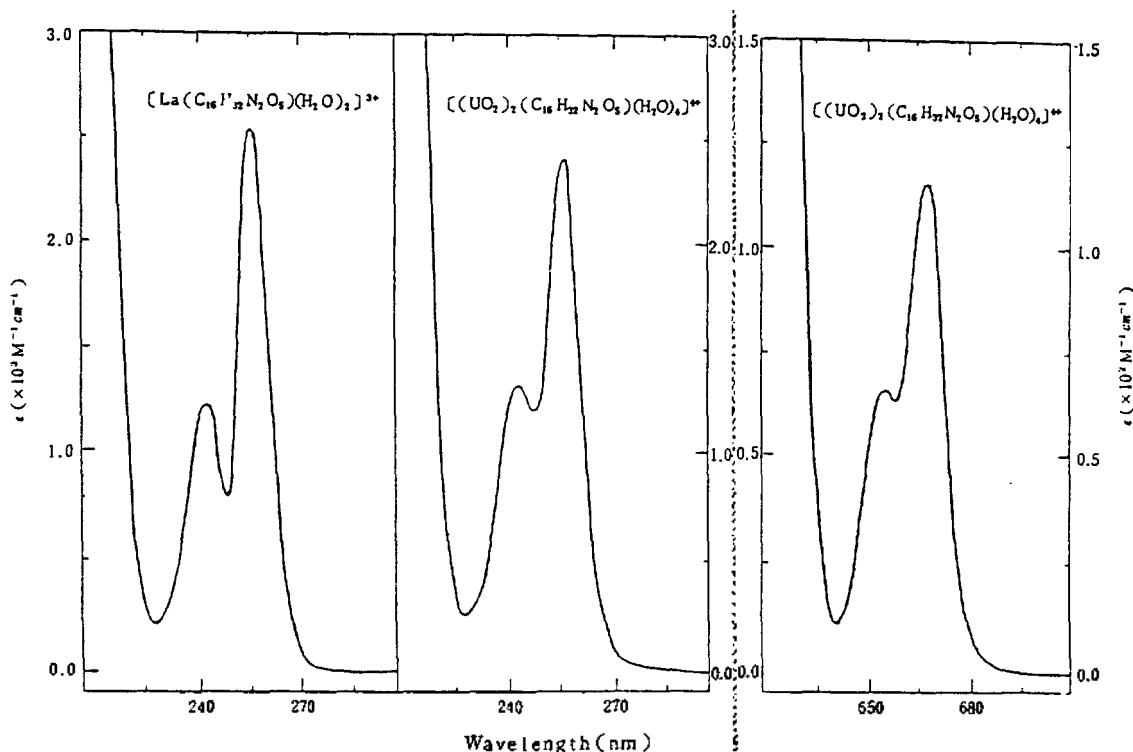


Figure 5. UV-Vis. spectra of lanthanides(III) and dioxouranium(VI) nitrate complexes with cryptand 221.

Table 5. UV-Vis. Spectra of UO_2^{2+} and Rare Earth Metal Ion Complexes with Cryptand 221 in Demethylformamide(DMF) Solution

complexes	wavelength (nm)	molar absorptivity (1/M. cm)
UO_2^{2+}	673.8, 656.2	115, 68.0
	253.8, 244.2	2430, 1318
La^{3+}	258.6, 243.7	2520, 1260
Pr^{3+}	257.1, 243.6	2460, 1140
Ho^{3+}	255.8, 239.4	2320, 1038

tive coefficients calculated in methanol, acetonitrile and acetone solution are shown in Table 4. It is seen that the selectivity is dependent on the solvent, and the selectivity order of the solvents increase in the following order: $\text{CH}_3\text{COCH}_3 > \text{MeOH} > \text{CH}_3\text{CN}$. We have also shown that in the case of cryptand 221, the $K_{\text{UO}_2^{2+}}/K_{\text{La}^{3+}}$ ratio is much higher than the $K_{\text{La}^{3+}}/K_{\text{Pr}^{3+}}$ in the same solvent.

Electronic Spectra. The electronic spectra of the metal complexes with cryptand 221 are shown in Figure 5, and the summary of the electronic spectra of the cryptand 221 and related complexes are given in Table 5. The two-band spectrum of cryptand 221 complex is a typical form of macrocycles series.

The major difference in the spectra as the size of metal ions changes is a loss of depth in the minimum between two peaks, and also the absorptive wavelengths of lanthanide (III) complexes appear in 230-260 nm, whereas those of the dioxouranium(VI) complex appear in 230-260 and 640-675 nm.

The complexation with lanthanides(III) or dioxouranium

Table 6. Log K , ΔH (Kcal/mol) and ΔS (cal. deg. mol) for the Interaction of Cryptand 221 with Metal Ions at $25 \pm 0.1^\circ\text{C}$ and $\mu=0.1$

Metal ion	ΔH	ΔS	Log K
La^{3+}	-13.6 ± 0.2	-1.8 ± 0.5	10.2 ± 0.3
Pr^{3+}	-12.4 ± 0.5	-2.3 ± 0.2	9.4 ± 0.6
Ho^{3+}	-5.8 ± 0.2	-2.5 ± 0.2	4.4 ± 0.1
UO_2^{2+}	-10.3 ± 0.2	-2.6 ± 0.3	7.7 ± 0.1

(VI) causes a blue-shift and an increase in the absorptive intensity for each transition except the band of UO_2^{2+} complex in the visible range. This trend has been observed in lanthanide(III) complexes with crownands²⁴ and is a clear indication of nitrogen atoms of the cryptand 221 being involved in bonding with metal ions.

In particular, such a electronic transition probably are exhibited at the tertiary amine nitrogens, rather than ether oxygen atoms, since solutions of the corresponding hydrated nitrates in dimethylformamide solvent do not exhibit electron-transfer bands in these spectral regions. These transitions can be attributed to electron transfer from the highest-energy molecular orbitals of the ligand to the 4f and 5f orbitals²⁵. The absorption bands (230-260 nm) of complexes which arise from the direct interaction of macrocycle donor atoms with the metal ions is $n \rightarrow \delta^*$ transition²⁶, and the absorption band (640-675 nm) of UO_2^{2+} -complex which arises from interaction between two-uranium(VI) metals existing outside the cavity of the ligand is $d \rightarrow d^*$ transition²⁶.

Thermodynamic Studies. Heat of dilution corrections were made by titrating solutions of the cryptand 221 or metal ion solutions into the methanol, and the method used to

calculate $\log K$ and ΔH values from the calorimetric data using a nonlinear least-squares techniques has been described by Eatough *et al.*²⁷

The ligand-cation systems in Table 6 illustrate in a systematic fashion the effect on cation binding of cryptand 221.

These data confirm the prevalent theory that correspondence of cation size to constant ligand ring cavity size (1.34–1.41 Å) is an important factor in determining the stabilities of complexes formed from cations small enough to enter the ligand cavity. The selectivity order of cryptand 221 in methanol is $\text{La}^{3+} > \text{Pr}^{3+} > \text{UO}_2^{2+} > \text{Ho}^{3+}$. The size of La^{3+} most closely corresponds to that of the ligand cavity, but the Ho^{3+} size is too small to enter the ligand cavity, and it can also be predicted that the stability constant of the UO_2^{2+} complex in methanol solution is decreased more than those of the La^{3+} and Pr^{3+} -complexes. The heat of UO_2^{2+} -complexes with crown ethers is produced but the complexes are not sufficient to calculate ΔH or $\log K$. By contrast, the macrocyclic ligand used in this study forms a considerably stable complex with UO_2^{2+} metal ion. The UO_2^{2+} ion as soft acid is strongly bonded with cryptand 221 rather than 18-crown-6. This trend is similar to those reported for the UO_2^{2+} -complexes of macrocyclic ligand with N_2O_2 donor set²³ and cryptand 222²⁹; therefore, it shows that the stability of this complex can relate to some characteristic for covalent bonding of nitrogen atoms as donors.

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