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Formation of Cadmium(II) Nitrate Complexes with Macrocycles

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The twelve macrocycle (L) complexes of cadmium(II) nitrate have been synthesized: $CdL(NO_3)_2$. All the complexes have been identified by elemental analysis, electric conductivity measurements, IR and NMR spectroscopic techniques. The molar electric conductivities of the complexes in water and acetonitrile solvent were in the range of 236.8-296.1 $cm^2 \cdot mol^{-1} \cdot ohm^{-1}$ at 25°C. The characteristic peaks of macrocycles affected from Cd(II) were shifted to lower frequencies as compared with uncomplexed macrocycles. A complex with 1,4,8,11-tetrakis (methylacetato)-1,4,8,11-tetraazacyclodecane (L_4) exhibited two characteristic bands such as strong stretching (1646 cm^{-1}), and weaker symmetric stretching band (1384 cm^{-1}). NMR studies indicated that all nitrogen donor atoms of macrocycles have greater affinity to cadmium (II) metal ion than do the oxygen atoms. The ^{13}C -resonance lines of methylene groups neighboring the donor atom such as N and S were shifted to a direction of high magnetic field and the order of chemical shifts were $L_1 < L_2 < L_3 < L_4 < L_5$. Also the chemical shifts values were larger than those of methylene groups bridgeheaded in side-armed groups. This result seems due to not only the strong interaction of Cd(II) with nitrogen donors according to the HSAB theory, but weak interaction of Cd(II) and COO^- ions or sulfur which is enhanced by the flexible methylene spacing group in side-armed groups. Thus, each additional gem-methyl pairs of L_3 , L_4 and L_6 macrocycles relative to L_1 , L_2 , and L_5 leads to an large enhancement in Cd(II) affinity. ^{13}C -NMR spectrum of the complex with L_{12} (1,5,9,13-tetracyclohexadecane-3,11 diol) reveals the presence of two sets of three resonance lines, and intensities of the each resonance line have the ratio of 1 : 2 : 2. This molecular conformation is predicted as structure of tetragonal complex to be formed by coordinating two sulfur atoms and the other two sulfur atoms which is affected by OH-groups.

Introduction

The 14-membered macrocycle, 1,4,8,11-tetraazacyclotetradecane^{1,2} (cyclam), has been the subject of numerous investigations. Cyclams are large enough to encircle a range of metal ions. X-ray diffraction studies confirm that *trans*-planar coordination occurs for this ligand in complexes of Ni(II), Ni(III), Co(II), Cu(II) and Tc(V). N-tetramethylated cyclam³ tends to promote the formation of five coordinate metal complexes. Thus, X-ray diffraction studies of $[NiLCl_3]$ and $[ZnLCl]^{+}$,⁴ indicate square pyramidal structures for these complexes with the monodentate ligands occupying axial positions.

The S_4 systems⁵⁻¹⁰ are the derivatives of a series of related S_4 -macrocycles having ring sizes between 12 and 16 members. As for the corresponding N_4 -analogues, this ligand series has been used to investigate the effect of ring size on the coordination behavior of this ligand type¹¹. Similarly, the mixed donor species¹¹⁻¹³ is a number of a related N_2S_2 -

series of macrocycles. These ligands have also been used to study the effect of ring and donor atom position on the complexation behavior of such ligands. Typically, double-armed crown ethers form encapsulated complexes with several metal cations and provide characteristic chemical function^{14,15}. Since high mobility of ligating pendant arms promises kinetically labile complexation, these armed macrocycles are recently recognized as the most suitable candidates for synthetic ionophores of metal cations.

The interaction between macrocycles and cadmium(II) compounds have not mostly been studied as compared with macrocyclic complexes with the other metals. This is unfortunate if one considers the importance of cadmium(II) as a polluting agent and its toxicologic aspects for living creatures. The design of synthetic receptors which could scavenge this element from industrial wastes or even from biological fluids need for a broader study of this field. The calculations reported by izatt¹⁶ for association constants of

Table 1. Analytical Data and Conductivity of Cadmium(II) Nitrate Complexes with Macrocycles

Complexes	Calc. (%)					Found (%)						
	C	H	N	S	Cd	C	H	N	S	Cd	NO ₃ ⁻	Λ
Cd(L ₁) (NO ₃) ₂	27.5	5.54	19.3	—	25.7	27.6	5.62	18.7	—	25.4	29.2	267.5
Cd(L ₂) (NO ₃) ₂	34.1	6.55	17.1	—	22.8	33.9	6.62	16.4	—	22.6	25.4	273.4
Cd(L ₃) (NO ₃) ₂	51.0	5.54	24.5	—	14.1	51.2	5.61	24.3	—	14.3	16.1	289.5
Cd(L ₄) (NO ₃) ₂	32.3	4.82	12.6	—	16.8	32.2	4.93	11.8	—	12.4	18.9	296.1
Cd(L ₅) (NO ₃) ₂	25.5	4.71	11.9	13.6	23.9	25.7	4.79	11.2	12.9	24.2	27.3	256.2
Cd(L ₆) (NO ₃) ₂	25.6	4.66	9.96	18.1	20.0	25.8	4.72	9.89	17.8	21.4	22.7	288.6
Cd(L ₇) (NO ₃) ₂	28.9	5.26	11.2	—	22.5	29.3	5.35	11.5	—	22.8	25.4	280.1
Cd(L ₈) (NO ₃) ₂	32.1	5.38	10.7	—	21.4	34.1	5.42	10.1	—	21.7	23.7	280.5
Cd(L ₉) (NO ₃) ₂	33.8	5.67	9.85	—	19.8	33.9	5.73	9.79	—	20.1	22.4	289.7
Cd(L ₁₀) (NO ₃) ₂	23.8	3.99	5.55	31.7	22.3	25.2	4.27	5.35	29.5	22.6	25.2	245.1
Cd(L ₁₁) (NO ₃) ₂	27.0	4.54	5.26	24.1	21.1	27.6	4.63	5.02	23.8	21.9	23.6	248.5
Cd(L ₁₂) (NO ₃) ₂	25.5	4.64	4.96	22.7	19.9	25.9	4.78	4.01	20.7	20.3	22.4	236.8

Λ: Molar Conductivity in water or acetonitrile solvents (CM²·M⁻¹·Ohm⁻¹).

cadmium(II) compounds with crown ethers in water, showed a very weak interaction. The presence of nitrogen atoms in the macrocycle clearly favoring the complexation of soft metals has been shown in several macrocyclic polyamines and cryptands. The results for the stable complexes of the macroheterocycles containing sulfur atoms and Cd²⁺ ion have also been described previously¹⁷. Nitrogen and sulfur donor atoms form stable complexes with transition and other heavy metal ions, while their complexes with the alkali and alkaline earth metals become less stable relatively to the corresponding macrocycles containing only oxygen donors¹⁸. Cryptands²⁰ of the N₂O₆ and N₂O₄ types with 2 or 3-pyridine and methylene groups tend to form stable complexes with a number of heavy metal ions. The particular interest is the selectivity of N₂O₄-macrocycles for Cd(II). The selectivity observed in the above case appears to arise because: (i) the nitrogen sites favour coordination of Zn(II) and Cd(II) relative to Ca(II) and (ii) the cavity-size favours coordination of Cd(II) relative to Zn(II).

We found the articles for complexation and structures of a number of other metal complexes except for Cd(II)-complexes with macrocycles. In this present papers, we undertook the synthesis of new cadmium(II) complexes with macrocycles of various types. Also we have investigated the structural characteristics of macrocycle complexes for Cd(II) by using the ¹³C and ¹H-NMR spectra, and FTIR spectra. The affinity of donor atoms to metal ions and changes in the planarity of macrocyclic ring upon the complexations of 14-membered macrocyclic series can have a substantial impact on chelation efficacy.

Experimental

Synthesis of Complexes. All of the cadmium(II) complexes with macrocyclic ligands such as 1,4,8,11-tetraazacyclotetradecane (L₁), 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (L₂), 1,4,8,11-tetrakis (2-pyridylmethyl)-1,4,8,11-tetraazacyclodecane (L₃), 1,4,8,11-tetrakis (methylacetato)-1,4,8,11-tetraazacyclodecane (L₄), 1,4-dithia-8,11-diazacyclodecane (L₅), 8,11-dimethyl acetato-8,11-dithia-1,4-diazacyclodecane (L₆),

1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (L₇), 4,7,13,18-tetraoxa-1,10-diazabicyclo [8,5,5] eicosane (L₈), 1,4,8,11-tetra-thiacyclotetradecane (L₉), 1,5,9,13-tetrathiacyclohexadecane (L₁₀), 1,5,9,13-tetrathiacyclotetradecane (L₁₁) and 1,5,9,13-tetrathiacyclohexadecane-3,11-diol (L₁₂) were prepared according to the methods of Nathamiel¹⁹, Poon²⁰, and Seminar²¹. A solution of 2.0 mmol ligand in 30 ml-solvents (methanol, acetonitrile and ethanol) was added dropwise to a solution of 3.0-4.5 mmole Cd(NO₃)₂ in 20 ml solvents under nitrogen atmosphere, and the mixture was stirred at 30°C for 24 hr. The polycrystalline complexes were filtered, washed with 30 ml CH₂Cl₂, dried in a desiccator over P₂O₅ for 2 days and under a vacuum (10⁻² Torr) during 3-10 days; yield 80-92% for each complex.

The data of elemental analysis of each complex were obtained by a Yamato C H N color and Thermo-Jeneral Ash Environ-II type ICP. The quantity of NO₃⁻ ion in each complex was determined by an orion 960 auto chemistry system equipped with a NO₃⁻ ion selective electrode, and the molar conductivities²² of the complexes were measured with a Kyoto electric CM-70 digital conductivity bridge.

Proton NMR Measurements. Proton NMR measurements were carried out on a Varian Gemini 200 and 300 MHz spectrometer. The NMR solvent was acetonitrile-d₃, and chemical shifts were referenced to TMS.

Carbon-13 NMR Measurements. 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 rock. 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.

IR Spectra. The IR-Spectra were obtained from KBr pellets on a Perkin-Elmer 1600 FT IR spectrophotometer.

Results and Discussion

Elemental Analysis and Conductivity. The analytical data of elements and results of conductivity of the com-

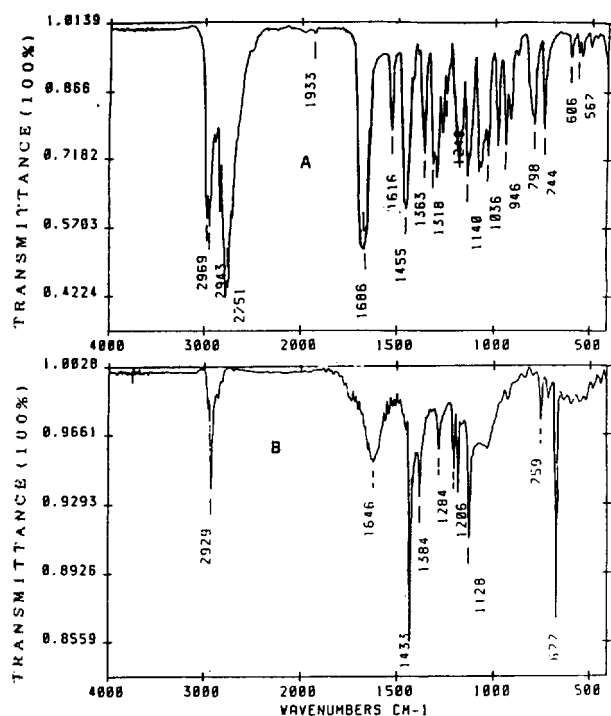


Figure 1. IR-spectra of macrocycle 4 (L_4) and its complex (B).

plexes were shown in Table 1.

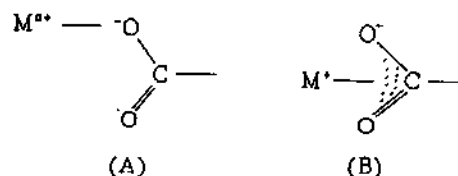
All of the complexes of cadmium(II) with macrocycles (L_1 - L_{12}) are not hygroscopic and all complexes have 1:1 stoichiometry. The complexes with L_1 - L_9 are soluble in water and that with L_{10} - L_{12} are soluble in acetonitrile solvent.

The molar electric conductivities of the complexes in water and acetonitrile were in the range of 236.8-296.1 $\text{cm}^2 \text{mol}^{-1} \text{Ohm}^{-1}$ at 25°C. Therefore, all complexes have been dissociated as 1:1 electrolytes²² in acetonitrile and water solvent. Also the NO_3^- ion content measured by ion selective elec-

trode method was conformable to theoretical values.

IR Spectra. The infrared spectra (IR) of the macrocycle (L_4) and its complex were representatively given in Figure 1. The principal characteristics spectral patterns were also listed in Table 2. The IR bands exhibited by the ligands which undergo significant changes on complexation with metal ions were arising from C-N-C, C-O-C, C-S-C and R-COO⁻ stretching and CH₂ bending vibration modes. The C-N-C, C-O-C and C-S-C stretching modes which show strong and sharp bands around 1128-1121, 1056, 1220-1130, 850 and 839 cm^{-1} in the spectra of the free ligands, were shifted upon complexation about 65-10 cm^{-1} to lower frequencies. Also the CH bending modes which appear at 1053-950 cm^{-1} in the spectra of the ligands were shifted upon the complexation to lower frequencies.

These spectral changes are similar to those reported for the lanthanides(III) nitrate complexes with 1-10-diaza-18-crown-6, cryptand 221 and other cryptand series²³. Only bands arising from the C_{2v} symmetry nitrate group appear at 1384 and 1433 cm^{-1} of the nitrate complexes with these macrocycles. These bands due to the ν_3 mode suggest ionization of nitrate group. A free carboxylate ion^{24a} of the L_4 exhibits two bands: a strong stretching band (ν_{AS}) between 1686 and 1616 cm^{-1} and a weaker symmetric stretching band (1455 cm^{-1} , ν_S) and the carboxylate mode of the complex with L_4 exhibited at 1646 and 1384 cm^{-1} . Interactions of metal ion and a carboxylate ions occur with a variety orientation^{24b}:



The type A interaction will increase ν_{AS} toward the frequency of a carbonyl group, while ν_S will fall toward the frequency of a C-O group^{24b}. As a result, $\Delta\nu = \nu_{AS} - \nu_S$ will

Table 2. Guest (Cd^{2+}) Induced Changes in Characteristic Infrared Shifts (cm^{-1}) of Macrocycles

Bands	Assignments (cm^{-1})							
	Ligand	Complex						
		1	2	3	4	9	10	12
NH	1558 _(s)	1497 _(w)	N	N	N	N	N	N
C-N-C	1128-1121 _(s)	1096 _(w)	1098 _(w)	1086 _(w)	1088 _(w)	1091 _(w)	N	N
N-CH ₂	1249 _(m)	N	1213 _(m)	1224 _(m)	1221 _(m)	N	N	N
	2965 _(s)		2958 _(m)	2942 _(m)	2948 _(m)	2934 _(m)		
R-Py	648 _(m)	N	N	642 _(m)	N	N	N	N
	476 _(w)	N	N	461 _(m)	N	N	N	N
R-COO	1686 _(s)	N	N	N	1646 _(m)	N	N	N
C-S-C	850 _(m)	N	N	N	N	N	839 _(w)	814 _(w)
R-O-R	1056 _(s)	N	N	N	N	1042 _(w)	N	N
Cd-O	—	N	N	N	567 _(w)	485 _(w)	—	—
Cd-N	—	275 _(m)	258 _(m)	252 _(m)	255 _(m)	258 _(m)	—	—
Cd-S	—	—	—	—	—	—	453 _(m)	474 _(m)
OH	3295 _(s)	—	—	—	—	—	—	3241 _(m)

N: No detection.

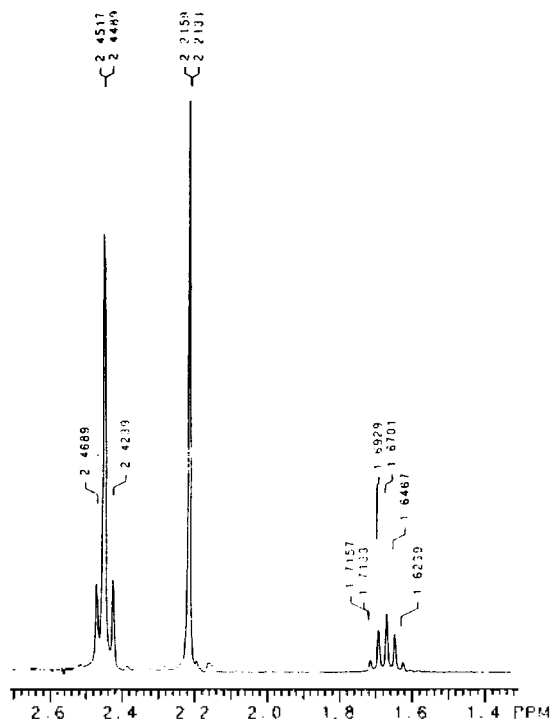


Figure 2. $^1\text{H-NMR}$ Spectrum of Cd^{2+} Complex with Macrocycle 2.

measure the symmetry of the metal-carboxylate interaction. A $\Delta\nu$ greater than 225 cm^{-1} show the characteristic of the tight symmetry of the type (A), while values of $\Delta\nu$ lower than 224 cm^{-1} indicate a looser symmetric interaction of type (B). Our key bands were shown in Figure 1. The stretching bands of the complex results in the shift of the carboxylate band to 1646 cm^{-1} in the range of typical of ν_{AS} and the other band (ν_{S}) shifts to 3184 cm^{-1} . The difference of the value (262 cm^{-1}) is suggested as interaction of type (A). The similar results are reported for Na^+ and Ca^{2+} complexes with ButyINH18C6 ligand²⁵.

Only OH stretching vibration (3241 cm^{-1}) band appears in the complex with L_{12} . This band was shifted to the direction of long wavenumber for the complex. Thus, this is suggested in a band due to the twist vibration of OH-groups attached to macrocyclic ring.

The metal-to-donor atom bands were listed in Table 2. The metal-to-oxygen and metal-to-sulfur bands which appear upon complexation at $465, 453$ and 474 cm^{-1} exhibited at higher frequencies than metal-to-nitrogen band. These types of bands were similar to those reported for the other complexes with cryptand 221 and noncyclic ligands²⁶, and the bands of red shift which appears at $294, 290$ and 252 cm^{-1} is considered to be diagnostics of amide coordination for a Lewis acid through the nitrogen atom in the ligand.

Proton NMR Spectra. We determined the relative affinities of macrocycles, L_1 - L_{12} , for $\text{Cd}(\text{II})$ in acetonitrile- d_3 by $^1\text{H-NMR}$ spectrometer. Solutions containing 1 equiv. of the macrocycles and 1 equiv. of $\text{Cd}(\text{II})$ were examined after equilibrium had been reached after several days at room temperature. Signals for metal-bound and metal-free forms of macrocycles were observed in case.

The proton NMR spectra of complexes with macrocycles were given in Figure 2-4, and the proton chemical shifts

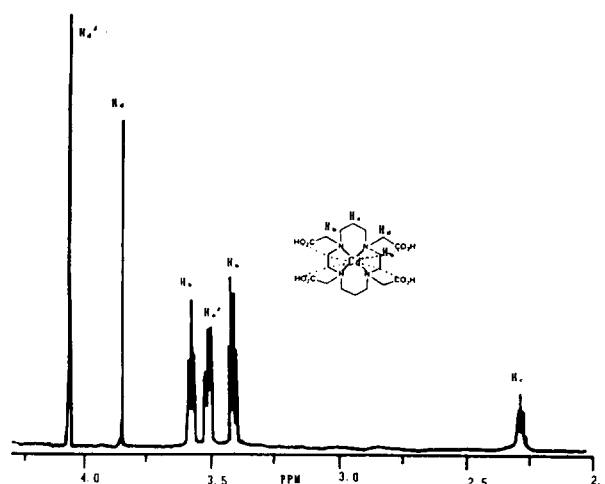


Figure 3. $^1\text{H-NMR}$ Spectrum of Cd^{2+} Complex with Macrocycle 4.

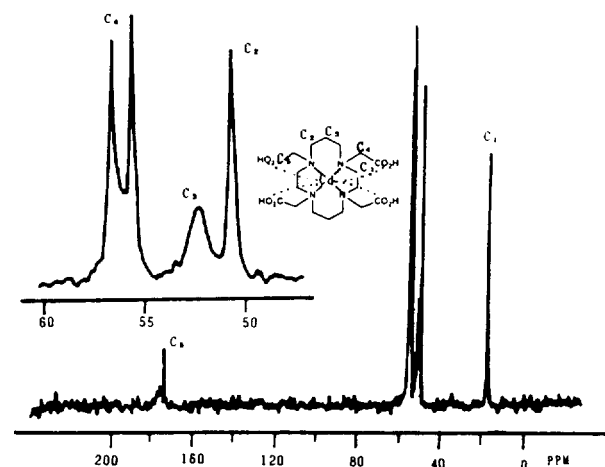


Figure 4. $^{13}\text{C-NMR}$ Spectrum of Cd^{2+} Complex with Macrocycle 3.

for the complexes were listed in Table 3-5. The chemical shifts for neighboring protons of OCH_2 group were nearly constant, while all of the methylene proton resonance lines for CH_2NH , and SCH_2 being around nitrogen of sulfur donor atoms were shifted to downfield (Table 3-5).

These proton-resonance line were shifted to downfield frequencies, because the electronegativity of the donor atoms are increased by interaction of metal cation and donor atoms such as nitrogen and sulfur³². Thus, these complexes were mostly formed by donating the nonbonding electron pairs of the nitrogen or sulfur atom.

The proton spectra of the complex ion containing L_4 and $\text{Cd}(\text{NO}_3)_2$ (Figure 3) showed the triplet and quintuplet signals of the side-armed carboxylate and macrocycle. Both of these signals were well resolved in the range of 2.26-4.10 ppm and were well separated from the other methylene signals being around tetra-nitrogen atoms. Therefore, carboxylate signals were used to the probe monitoring the complexation. The proton signals of the methylene groups of macrocycles were well separated as sharp quintuplet (H_a), triplet (H_b) and triplet (H_c) at 2.52, 2.26 and 3.64 ppm, respectively. Also proton signals of side-armed methylene group were well separated as the singlet at 3.82 and 4.09 ppm. These peaks

Table 3. Guest (Cd^{2+}) Induced Changes in Principal $^1\text{H-NMR}$ Chemical Shifts of Macrocycles 1,5,7,8 and 9

Ligands	1			5			7			8			9		
Protons shifts values (ppm)	H_a	H_b	H_c	H_a	H_b	H_c	H_a	H_b	H_c	H_a	H_b	H_c	H_k	H_m	H_n
	0.19	0.07	0.02	0.14	0.04	0.06	0.08	0.03	0.01	0.09	0.04	0.02	0.17	0.05	0.02

Table 4. Guest (Cd^{2+}) Induced Changes in Principal $^1\text{H-NMR}$ Chemical Shifts of Macrocycles 1,2,3,4 and 6

Ligands	1			2			3			4			6		
Protons	H_a	H_b	H_c	H_a	H_b	H_c	H_a	H_{1b}	H_{1c}	H_a	H_b	H_c	H_a	H_b	H_c
Ligand (ppm)	2.35	3.18	1.64	2.36	3.20	1.62	3.57	3.48	2.19	3.41	3.59	2.20	2.41	2.61	1.82
Complex (ppm)	2.42	3.20	1.65	2.45	3.23	1.67	3.67	3.52	2.21	3.52	3.64	2.26	2.48	2.63	1.83
Shift (ppm)	(0.07)	(0.02)	(0.01)	(0.09)	(0.03)	(0.01)	(0.10)	(0.04)	(0.02)	(0.11)	(0.05)	(0.02)	(0.07)	(0.02)	(0.01)

Table 5. Guest (Cd^{2+}) Induced Changes in Principal $^1\text{H-NMR}$ Chemical Shifts of Macrocycles 10,11 and 12

Ligands	10			11		12		
Protons	H_a	H_b	H_c	H_a	H_b	H_a	H_b	H_c
Ligand (ppm)	3.31	3.65	3.18	3.31	3.66	0.94	2.47	0.42
Complex (ppm)	3.37	3.68	3.19	3.40	3.69	0.98	2.49	0.37
Shift (ppm)	(0.06)	(0.03)	(0.01)	(0.09)	(0.03)	(0.04)	(0.02)	(-0.05)

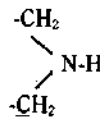
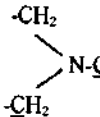
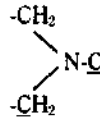
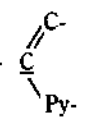
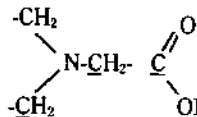
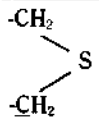
were observed as the downfield shifts H_a and H_b methylene protons formed coupling. The coupling constants of complex were more decreased than those of ligands. These peaks were weakly shifted to downfield direction as compared with the peaks of uncomplexed L_4 . Thus, it seems that carboxyl group has a weak interaction for the metal ion. The acetate protons coalesce into sharp single peak, and a AA'BB' splitting pattern was observed for the ethylene group. The two proton peak of AA'BB' splitting pattern was thus expected for the H_1 - H_2 and the H_3 - H_4 pairs in agreement with the observed spectra. The same result is observed for lanthanide (III) complex with L_4 ²⁷.

The proton spectra of the complex ions containing cryptand series (L_7 , L_8 and L_9) showed different methylene sig-

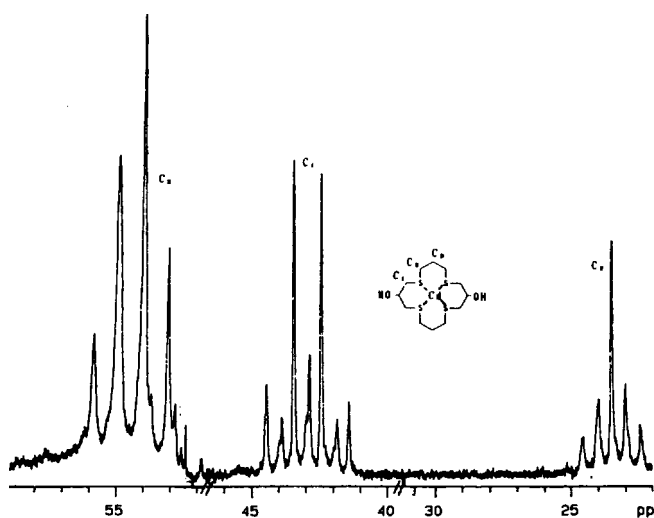
nals each other. These methylene signals were well separated in sharp peaks in the range of 1.09 and 2.59 for L_7 , and 2.6-3.2 and 3.85 ppm for L_9 . In the presence of the L_7 -complex, the upfield shifts of up to 0.08 ppm (24 Hz) were observed. However, in the presence of the L_8 and L_9 -complex, the downfield shifts of 0.09 (37 Hz) ppm and 0.17 (51 Hz) ppm were observed. These differences for the chemical shifts change is understood by considering the differences for the structures of L_7 , L_8 and L_9 .

The proton spectra of the complex ions containing thioether series (L_{10} - L_{12}) showed each different methylene signals. The proton signals of the methylene were well separated in sharp peak in the range of 3.19, 3.37 and 3.68 for L_{10} , 3.21, 3.38 and 3.69 for L_{11} and 0.37, 0.98 and 2.50 ppm for

Table 6. Guest (Cd^{2+})-Induced Changes in ^{13}C -NMR Chemical Shifts of Macrocycles 1,2,3,4 and 6

Ligands	Guest (Cd^{2+})-Induced shifts values (ppm) ^a									
										
1	-0.2	-	-	-	-	-	-	-	-	-
2	-	-0.7	-0.2	-	-	-	-	-	-	-
3	-	-	-	-0.9	-0.3	-0.4	-	-	-	-
4	-	-	-	-	-	-	-1.7	-0.3	-0.5	-
6	-	-	-	-	-	-	-1.2	-0.2	-0.2	-0.6

Ligands, 0.050 mmol; Cadmium nitrate, 0.050 mmol in DMSO-MeOD (3:1), ^a-means up-field shift calculated from averaged shifts of complex and ligand.

**Figure 5.** ^{13}C -NMR Spectrum of Cd^{2+} Complex with Macrocycle 12.

L_{12} .

The proton NMR spectra of the complexes with L_{10} and L_{11} were similar to each other, but the proton spectra of the complex with L_{12} showed different mode as compared with those of the complexes with L_{10} and L_{11} . The chemical shifts were listed in Table 5. Only proton spectra neighboring S- CH_2 were shifted to downfield. However, the proton signal (H_c) of L_{12} having an electron affinity group such as OH was shifted to the direction of upfield because the deshielding zone of the hydroxyl group covers the macrocyclic ring.

^{13}C -NMR Spectra. The ^{13}C -NMR spectrum for the Cd^{2+} complex with side-armed macrocycles, L_4 was given in Figure 4.

Figure 4 shows the methylene carbon signal of the ^{13}C -NMR spectrum. The carboxylate band coordinated near 178 ppm appeared in this complex. The result indicates that $\text{Cd}(\text{L}_4)$ complex in acetonitrile- d_3 exists as complex ions occupying both macrocyclic ring and the carboxyl groups of L_4 . Thus, this complex has both chelate and macrocyclic effects.

^{13}C -NMR chemical shifts of $\text{Cd}(\text{II})$ complexes with macrocycle (L_1 , L_2 , L_3 , L_4 and L_6) were listed in Table 6. The ^{13}C -resonance lines of methylene neighboring the donor atom such as N and S were shifted to a direction of high magnetic field in the range of 1.7-0.2 and the order were $\text{L}_1 < \text{L}_2 < \text{L}_6 < \text{L}_3$

$< \text{L}_4$. Also these shifts were larger than the shifts of methylene-carbon bridgehead in side-armed groups. The order of these shifts coincided with those of stability constants discussed previously²⁸. The ^{13}C -NMR spectrum of $[\text{Cd}(\text{L}_{12})](\text{NO}_3)_2$ complex was shown in Figure 5. The structure of L_{12} is differently from L_{10} and L_{11} of the thioether series. Thus, it is expected that this complex has different structure as compared with the complexes with L_{10} and L_{12} .

For the centrosymmetric structure, only three resonance lines are expected with relative areas ratio of 1:2:2. The ^{13}C -spectrum of $[\text{Ni}(\text{L}_{10})(\text{BF}_4)_2]$ reveals the presence of two sets of three resonances at 298 K²⁹. Also ^{13}C -NMR spectrum of the complex with L_{12} reveals the presence of two sets of three resonance lines, and the intensity-ratios was 1:2:2. This structure is consistent with ligand-conformation predicted in tetragonal complex²⁹. Thus, this molecular conformation would be also predicted as structure of the complex to be formed by coordinating two sulfur atoms and the other two sulfur atoms which is affected by OH groups.

Cram pointed out that a variety of factors can contribute to strong "host-guest" interactions³⁰. Structural flexibilities may play a role in the improvement in $\text{Cd}(\text{II})$ binding observed for L_3 , L_4 , and L_6 relative to L_1 , L_2 , and L_5 . The enhanced chelation could also result from the strain built in L_3 , L_4 , and L_6 by incorporating the geminal-methyl groups. Thus, each additional gem-methyl pair leads to an enhancement in $\text{Cd}(\text{II})$ affinity. ^1H and ^{13}C -NMR studies indicated that relative binding affinity of the donor atoms for cadmium(II) was increased in order of $\text{N} > \text{S} > \text{O}$. Thus, this result coincide with HSAB theory³¹.

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Electrochemical Behavior of Mordant Red 19 and its Complexes with Light Lanthanides

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Mordant Red 19(MR19) is reduced at mercury electrode at -0.67 V vs. Ag/AgCl with two electrons per molecule in pH 9.2 buffer by differential pulse polarography and linear sweep voltammetry. The peak potential is dependent on the pH of solution. The exhaustive electrolysis, however, gives 4 electrons per molecule because of the disproportionation of the unstable hydrazo intermediate. The electrochemical reduction of lanthanide-MR19 complexes is observed at more cathodic potential than that of free ligand. The difference in peak potentials between complex and free ligand varies from 75 mV for La³⁺ to 165 mV for Tb³⁺ and increases with increasing the atomic number of lanthanide. The electrochemical reduction of lanthanide complexes with MR19 is due to the reduction of ligand itself, and it can be potentially useful as an indirect method for the determination of lanthanides. The shape of *i*-E curves and the scan rate dependence indicates the presence of adsorption and the adsorption was confirmed by potential double-step chronocoulometry and the effect of standing time. Also the surface excess of the adsorbed species and diffusion coefficients are determined. The composition of the complex is determined to be 1:2 by spectrophotometric and electrochemical methods.

Introduction

Very similar electronic structure of lanthanides makes it difficult to separate one lanthanide from the others. The de-

velopment of simple and effective method of separation is still one of the challenging subjects in this field. The direct electrochemical reduction of lanthanides in aqueous media occurs at so negative potentials that hydrogen evolution in-