and Schmid.[10]

In the case of the sample obtained by calcining AS at 1250 °C for 20 h, there were no detectable peaks other than the peaks assigned to AlN in an XRD pattern, as shown in Figure 1(b). Each peak in Figure 1(b) is much broader than in Figure 1(a), but in the ^{27}Al magic-angle spinning (MAS) NMR spectrum only one peak at 114 ppm which is assigned to AlN[13] had almost the same linewidth (1.2 kHz) as that of the sample prepared at 1500 °C for 20 h. No whiskers were formed in the sample, indicating that the calcination temperature is very important for formation of AlN whisker. More detailed studies on the nucleation and growth of AlN whisker from basic dicarboxylate Al(III) complexes are in progress in order to elucidate the whisker growth mechanism, determine the optimum conditions for whisker growth, and synthesize larger single crystals.

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11. The AG complex was prepared by the same method as described in Ref. 6. Its empirical formula was determined by thermal analysis, gravimetry, IR, ^{27}Al MAS NMR and ^{13}C CP/MAS NMR spectroscopy. Details on synthesis of AlN using AG will be in preparation for publication.
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The Multinuclear NMR Study for the Coordination Number of the La(III) Complex of Triethylenetetraaminehexaacetic Acid(TTHA) in Aqueous Solution

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Lanthanide complexes of polyaminopolycarboxylic acids are being employed extensively in magnetic resonance as MRI contrast reagents and as shift reagents for alkali metal nuclei.[1] Although many ligands have been used for these purposes, the most useful of these ligands is triethylenetetraaminehexaacetic acid (TTHA).[2] On the other hand, only are there two diamagnetic nuclei, lanthanum($^{139}La^{3+}$) and lutetium($^{175}Lu^{3+}$), in lanthanides for the study of the coordination properties of cations especially for the NMR spectroscopy study. Although trivalent lutetium($^{175}Lu^{3+}$) has I=7/2 and 97.41% of natural abundance, its nuclear quadrupole moment(Q) is about 27 times bigger than that of lanthanum($^{139}La^{3+}$) (quadrupole moments are 5.68 and 0.21 barns, respectively).[3] Since the NMR linewidth ($\upsilon_{1/2}$) is proportional to the square of quadrupole moment, we can easily predict the linewidth of Lu to be several 10^4-10^5 Hz in terms of known ^{139}La linewidth.[4] From this practical point of view, lanthanum($^{139}La^{3+}$), which has I=7/2 and 99.1% of natural abundance, appears to be only one of the NMR plausible nuclei in lanthanides. In practice, lanthanum(III) cations already have been proposed as model for Ca^{2+} binding sites to study coordination properties in proteins[5] and ^{139}La NMR has been used for the analytical tool of relevant nucleus.[3]

In order to understand the interplay between polydentate coordination of the ligand with lanthanum and the availability of charged carboxyl sidechains acting as cation attractors, the determination of complex structure is prerequisite. It has been previously known using ^1H NMR that EDTA (ethylenediaminetetraacetic acid) and DTPA (diethylenetriaminepentaacetic acid) have 6 coordination numbers (2 nitrogens and 4 carboxylates) and 7 coordination numbers (3 nitrogens and 4 carboxylates) with alkaline earth and diamagnetic lanthanide cations (La^{3+}, Lu^{3+}, and Y^{3+}), respectively.[6] However, in the case of TTHA complex, the structure has never been studied completely and even the coordination number is still controversial. More specifically, there are two proposals: one with eight coordination number (4 nitrogens and 4 carboxylates)[7] and the other involving six coordination number (2 nitrogens and 4 carboxylates).[4] The fact that TTHA ligand can not donate all 10 possible donor atoms is well supported by the ligand-induced ^{139}La NMR chemical shift.[4]

The present communication reports the results of the ^1H

(COSY and long-range COSY), ^{13}C (CH-HETCOR and long-range CH-HETCOR), ^{15}N, and ^{139}La NMR experiments of a solution of the K^+ salt of $\{TTHA[La(III)]\}^{3-}$ complex in D_2O aiming at the determination of the proposed coordination numbers and generalized ligand-induced shifts.

A 0.1 M sample of $K_3LaTTHA$ in 99.9% D_2O was prepared by dissolving one equivalent of $LaCl_3$, one equivalent of H_6TTHA, and six equivalents of KOH with warming. Because of the method of preparation, the solution also contained 0.3 M KCl. Several hours was required to achieve a homogeneous solution. Spectra of the free ligand were obtained on an identical solution prepared without the addition of the $LaCl_3$.

NMR spectra were recorded using a Bruker AMX-500 spectrometer. ^1H (500.13 MHz), ^{13}C (125.76 MHz), and 2D spectra were obtained using a 5 mm dual probe. ^{15}N (50.68 MHz) and ^{139}La (70.66 MHz) were obtained using a 10 mm broadband probe and broadband preamp. All but the ^{139}La spectrum were obtained at 22 °C. The latter was obtained at 64 °C for comparison with literature values of the linewidth and chemical shift. For the variable temperature experiment, the probe was heated by a Bruker B-VT 1000E and allowed to equilibrate at each temperature before acquisition.

^1H spectra were referenced to internal HOD, assumed to be at 4.63 ppm by comparison with an external HOD sample. ^{13}C spectra were referenced to added dioxane, ^{15}N spectra were referenced to external nitromethane and ^{139}La to external $La(aq)^{3+}$ contained in a coaxial capillary. Energy minimization was explored on a Macintosh computer using the MM2 method in the Chem-3D model building program.

The observed ^1H spectra showed that a 0.1 M solution of $K_3[(TTHA)La(III)]$ in D_2O at room temperature was a single chemical species (Attempts to form the analogous complex of either the Lutetium or Yttrium, however, seem to yield overlapping spectra from several species). Although the widths of some ^{13}C peaks were significantly broadened at room temperature, the high temperature study showed that the widths of ^{13}C peaks were temperature dependent suggesting the incompletely averaged structures at room temperature. The linewidth variations of ^1H and ^{13}C NMR spectrum of this complex at room temperature suggest that the structure represents an average among structures or conformations with lower symmetry. MM2 minimization also yields several asymmetric structures with lower steric energies than the symmetrical structure. Similar linewidth effects, arising from conformer interconversions, have been reported[8] for the related lanthanide complexes of 1,4,7,10-tetraazacyclododecane-N,N',N",N'"-tetraacetic acid.

The analyses of the COSY and CH-HETCOR suggest that this solution are consistent with a species which has an average structure with two-fold symmetry, as indicated by the presence of only six types of methylene and three types of acetate groups. The CH-HETCOR spectrum of this complex is shown in Figure 1. All six types of methylene carbons have AB types of protons which also show strong scalar coupling on COSY spectrum.

Although the exact mechanism and quantity of the downfield chemical shift are not known when the nitrogen is coordinated with transition metal, Figure 2 clearly shows that two types of ^{15}N (δ, -329.4 and -338.9) were shifted to downfield (14.9 and 12.8 ppm, respectively) relative to the free ligand. This also suggests a species which has a two-fold symmetry relative to nitrogens coordination and has 4 nitrogens coordination. This phenomenon of downfield shift is similar to the ^{15}N shift reported for the Hg(II)

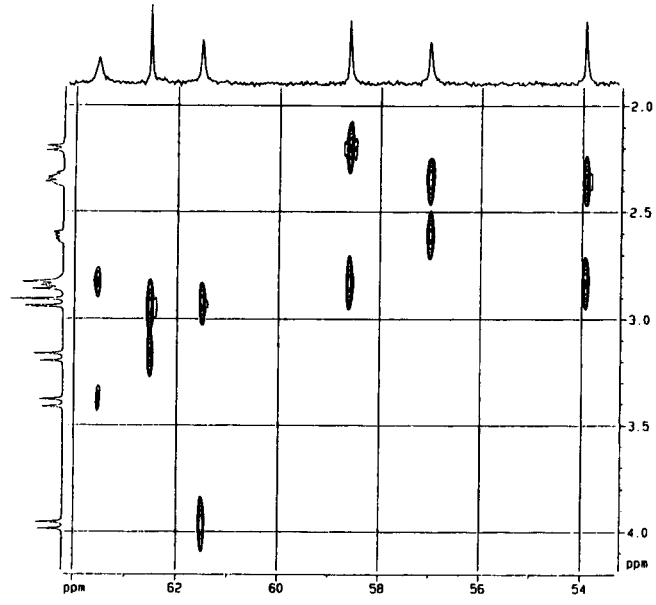

Figure 1. 2D CH-HETCOR spectrum of 0.1 M solution of LaTTHA at 125.76 MHz. The data were acquired with 512×64 data points and followed by zero-filling to give 1 k×256. F2 and F1 dimensions were filtered by exponential (LB=2) and sine-squared functions and followed by magnitude calculation, respectively.

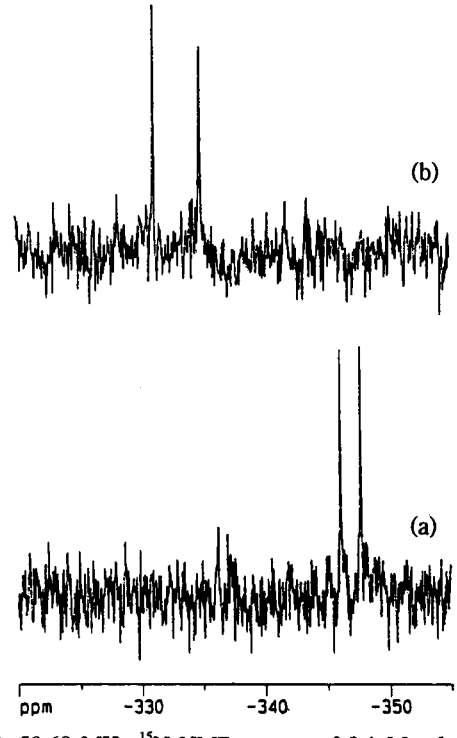

Figure 2. 50.68 MHz ^{15}N NMR spectra of 0.1 M solution of (a) K_6TTHA, (b) LaTTHA. Line broadening was done by Lorentz multiplication (LB=2 Hz) of the FID prior to Fourier transformation and baseline correction was done by 5 degree of polynominal function.

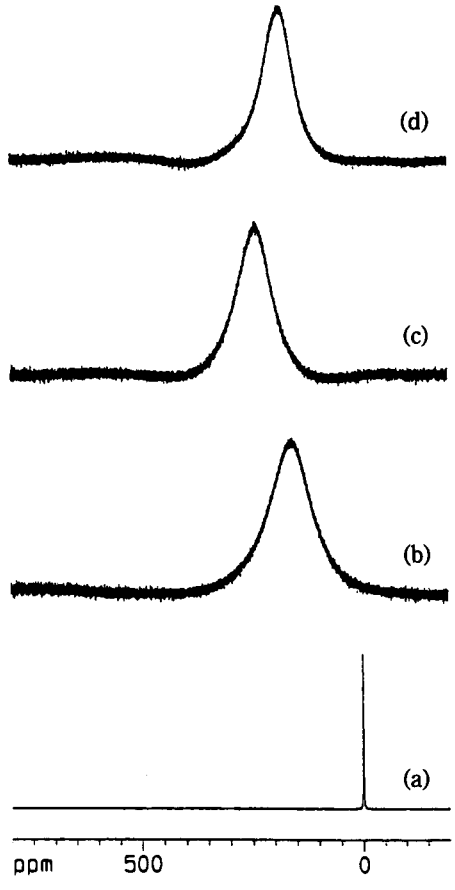

Figure 3. 70.66 MHz ^{139}La NMR spectra of 0.1 M solution of (a) La(aq)$^{+3}$, (b) LaEDTA, (c) LaDTPA, (d) LaTTHA. Line broadening was done by Lorentz multiplication (LB=1 Hz) of the FID prior to Fourier transformation and baseline correction was done by 5 degree of polynominal function.

complex of EDTA[9] and Y(III) complexes of EDTA and DTPA.[10]

The ^{139}La NMR spectra of this complex with LaEDTA and LaDTPA complexes are shown in Figure 3. The ^{139}La chemical shift of the complex relative to external La^{3+}(aq) at 64 °C is 185±1 ppm with an observed linewidth of 6500± 100 Hz. Previously reported value is 224±2 ppm and 5570 Hz under similar conditions,[4] and interpreted as favoring a structure involving coordination of only two nitrogens. The ^{139}La chemical shift (185 ppm) is in the middle of the chemical shift of two complexes (LaEDTA; 158 ppm, LaDTPA; 240 ppm) as shown in Figure 3. The observed chemical shifts are significantly different from the literature values, but the trend of chemical shift is the same as the reported results. It has been known that EDTA and DTPA have 6 coordination (2 nitrogens and 4 carboxylates) and 7 coordination (3 nitrogens and 4 carboxylates), respectively.[4,6] This suggests with the ^{15}N NMR result that the previous two proposals about the number of coordination should be modified. Because the ^{15}N NMR result confirms the 4 nitrogens coordination, two carboxylates can only be coordinated to lanthanum to explain the ^{139}La chemical shift and two-fold symmetry.

In conclusion, this preliminary report presented the new coordination of LaTTHA^{3-} complex and gave the evidence that the ligand induced shift for lanthanum complexes should be reinvestigated. Future studies based on the observation of well-resolved spectra from LaTTHA^{3-} should make it possible to combine related techniques to fully characterize the 3-D structure of this complex and to understand the roles of cation attractor. Further progress will be reported in due course.

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