Yttrium-89 and Nitrogen-15 NMR Spectroscopy of Yttrium Complexes of Polyaminocarboxylic Acids: Promising New NMR Parameters

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The chemistry of yttrium has known as a model for lanthanoid analogues.[1] Although yttrium is not formally a lanthanide element, its +3 oxidation state and similar radial size (the ionic radii of Er^{+3} and Y^{+3} are 0.881 and 0.88 Å, respectively) have rendered it for a good candidate to study chemical and structural problems of lanthanides. Especially for the NMR spectroscopy study, only are there two diamagnetic nuclei, lanthanum ($^{139}La^{+3}$) and lutetium ($^{175}Lu^{+3}$), in lanthanides. Although trivalent lutetium ($^{175}Lu^{-3}$) has I=7/2 and 97.41% of natual 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).[2] Since the NMR linewidth ($v_{1/2}$) 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.[3] 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, ^{139}La NMR has been used for the analytical tool of relevant nucleus.[2] For the NMR investigation, yttrium has additional advantages over the lanthanum. In addition to chemical shifts, the nuclear spin-spin coupling constant is a very valuable information about the chemical bonding. This nuclear spin-spin coupling can be measured from the NMR spectrum of either nucleus between the covalent bond. However, if either spin has I>1/2, the signal will be too broad to measure small couplings due to quadrupolar relaxation pathways. While the lanthanum has the linewidth ($v_{1/2}$) from several hundreds to several thousands Hz,[3] the yttrium, which has I=1/2 and 100% of natural abundance, can provide valuable structural information *via* coupling constant to other I=1/2 nuclei such as ^{13}C, ^{31}P and ^{15}N. However, there have been relatively few reports of yttrium NMR because of the long T_1 relaxation times, low and negative magnetic moment, low receptivity, and low measuring frequency.[2] Some chemical shifts of yttrium salts, complexes, and organometallic compounds have been reported.[4,5] ^1H-^{89}Y, ^{13}C-^{89}Y, and ^{31}P-^{89}Y coupling constants have also been reported from the ^1H, ^{13}C, and ^{31}P spectra.[4,5,6]

The present work reports ^{89}Y chemical shifts and ^{89}Y-^{15}N coupling constants of aqueous yttrium complexes with ligands containing both nitrogen and oxygen atoms aiming at the possibility of studing ligand-induced chemical shifts and bonding effect.

0.1 M samples in 99.9% D_2O were prepared by dissolving one equivalent of $LaCl_3$, one equivalent of polyaminopolycarboxylic acids, EDTA (ethylenediaminetetraacetic acid), DTPA (diethylenetriaminepentaacetic acid), and TTHA (triethylene-

tetraaminehexaacetic acid), and four, five, and six equivalents of KOH by modified literature procedure.[3,7] Because of the method of the preparation, the solution of samples, KYEDTA (1), $K_2YDTPA(2)$, and $K_3YTTHA(3)$, also contained 0.3 M KCl.

NMR spectra were recorded using a Bruker AMX-500 spectrometer. ^1H (500.13 MHz) and ^{13}C (125.76 MHz) spectra were obtained using 5 mm probe and ^{89}Y and ^{15}N spectra were obtained at 24.5 MHz and 50.68 MHz using a 10 mm broadband probe at 22 ℃, respectively. ^{89}Y spectra were referenced to external $Y(aq)^{+3}$ and ^{15}N spectra were referenced to external nitromethane contained in a coaxial capillary. Because of the low natural abundance (0.37%) and long relaxation time for ^{15}N (delays between π/2 pulses were kept to 5 sec.), typical proton decoupled spectral acquisitions required overnight runs as expected. On the other hand, about one hour acquisitions of yttrium, which has known to have much longer T_1 (typically 40-60 sec. in 3 M nitrate solution),[4] gave enough signal to noise ratio (S/N=*ca.* 10, No. of scans=32, relaxation delay=120 sec.). When the 0.5 M solutions were used, 4 scans, which takes only 8 min. acquisition, gave about same S/N ratio as that of 0.1 M solutions. The typical linewidth ($v_{1/2}$) of yttrium complexes was 1.5-3 Hz.

The ^{89}Y NMR spectra of yttrium complexes, 1, 2, and 3 are shown in Figure 1 and ^{15}N NMR spectra of complexe 1 and 2 are shown in Figure 2 with the spectra of corresponding ligands. The values of chemical shifts of ^{89}Y and ^{15}N and one bond spin-spin coupling constants of $^1J_{Y-N}$ are listed in Table 1. The ^{89}Y chemical shift of YEDTA complex(1)
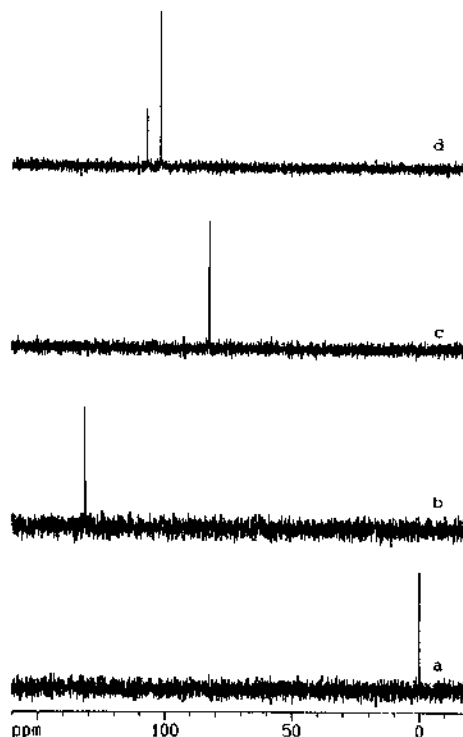
Figure 1. 24.5 MHz ^{89}Y NMR spectra of 0.1 M solution of a) $Y(aq)^{+3}$, b) YEDTA(1), c) YDTPA(2), d) YTTHA(3). Line broadening was done by Lorentz multiplication (LB=1 Hz) of the FID prior to Fourier transformation and baseline correction was done by 5 degree of polynorminal function.
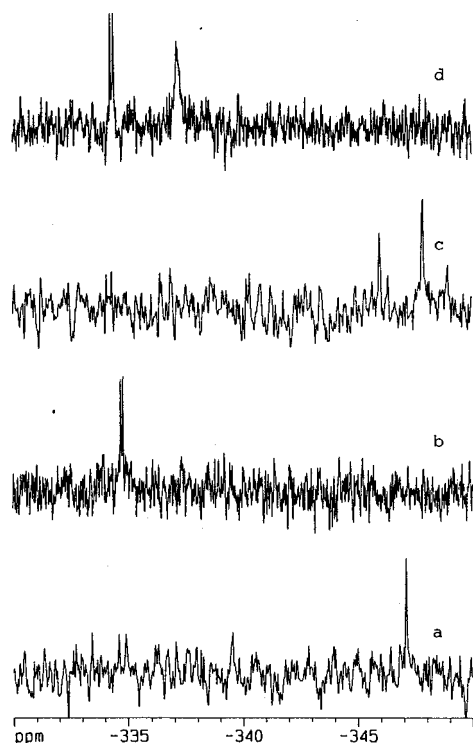
Figure 2. 50.68 MHz ^{15}N NMR spectra of 0.1 M solution of a) KEDTA, b) YEDTA(**1**), c) KDTPA, d) YDTPA(**2**). Line broadening was done by Lorentz multiplication (LB=1 Hz) of the FID prior to Fourier transformation and baseline correction was done by 5 degree of polynorminal function.

Table 1. ^{89}Y and ^{15}N NMR parameters for Yttrium complexes

Complex	^{89}Y/ppm[a]	^{15}N/ppm[b]	$^1J_{Y-N}$/Hz
1	131.3	−334.8 (−347.1)[c]	4.8
2	82.3	−334.3, −337.2[d] (−346.0, −347.8)[c]	6.2, 2.4
3	106.9, 101.6	−[e] (−331.1, −334.9)[c]	−[e]

[a] relative to 0.1 M Y(aq)$^{+3}$. [b] relative to nitromethane. [c] corresponding ligand (0.1 M potassium salt). [d] doublet-doublet peak at δ, −337.18 and −337.24. [e] could not be determined because of complexity.

are similar to those ascribed previously.[4]

It has been previously known using ^{1}H NMR that EDTA and DTPA 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.[7] In the case of TTHA complex, the fact that TTHA ligand can not donate all 10 possible donor atoms is especially supported by the ligand-induced ^{139}La NMR chemical shift.[3] More specifically, there are two proposals: one with eight coordination number (4 nitrogens and 4 carboxylates) and the other involving six

coordination number (2 nitrogens and 4 carboxylates).

The trend of the chemical shifts of ^{89}Y NMR clearly shows the ligand-induced shift in the EDTA and DTPA complexes. However, unlike the chemical shift of ^{139}La NMR, which is shifted to downfield depending on the increasing number of coordination, the chemical shift of ^{89}Y is shifted to upfield when the coordination number is increased. The ^{89}Y NMR of TTHA complex shows two different peaks with the integration ratio of 2 : 1. The ^{1}H, ^{13}C, and ^{15}N NMR of this complex(**3**) could not be read because of the overlapping in the spectra. However, in the ^{89}Y NMR, we can at least assume that this complex(**3**) has two different compounds. Although the coordination number of two different compounds could not be identified at this stage, the trend of chemical shift change which is in the middle of EDTA and DTPA complexes is same as that of corresponding lanthanum complexes.[3] Especially, the chemical shift change (40 ppm) with one additional nitrogen coordination between EDTA and DTPA complexes and the linewidth consideration (1.5-3 Hz) can clearly have advantage over the lanthanum chemical shift differences to distinguish unambiguously the coordination number of the unknown complexes.

The ^{15}N chemical shifts of complexes are shifted downfield by 12.3 ppm in EDTA complex(**1**) and 11.7 (middle nitrogen) and 10.6 ppm (terminal nitrogens) in DTPA complex(**2**) relative to the free ligands, respectively. This is smaller than the ^{15}N shift reported for the Hg(II) complex of EDTA but is larger than the shifts due to other divalent cations.[8] In addition to the chemical shift change which can provide a quite convenient model to study binding site, direct binding to the metal can be unambiguously concluded when one-bond coupling constants are observed. Although many of the important factors affecting the all types of spin-spin coupling are unanswered questions, the observation of scalar coupling in the metal-complex was used to provide an unequivocal information about the nature of ligands and their mode of binding.[9] The coupling constant ($^1J_{Y-N}$) of YEDTA(**1**) is 4.8 Hz and two different coupling constants, 6.2 Hz and 2.4 Hz, are observed for the YDTPA(**2**) complex. The coupling constants of 6.2 and 2.4 Hz in YDTPA complex(**2**) are assigned as those of the middle and terminal nitrogens in the molecule, respectively. The observed coupling constants ($^1J_{Y-N}$) are not able to answer whether this Y-N bonds of complexes is significant covalent or electrostatic. However, these coupling constants between yttrium and nitrogen are the first observed NMR parameters. In addition to the evidence of direct bonding of 3 nitrogens, the two slightly different chemical shifts of terminal nitrogens in YDTPA complex(**2**) are able to give the information that the conformation of the YDTPA complex in aqueous solution does not have two-fold symmetry. A further phenomenon observed in this study is the fact that the ^{15}N chemical shift change upon complexation, which is generally regarded as bond strength,[8] does not have any relationship with the corresponding size of coupling constants.

In conclusion, it is apparent that the ^{89}Y NMR together with ^{15}N NMR will provide more precise, convenient, and practical methods to study the coordination chemistry of lanthanides as a model and further progress will be reported in due course.

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