© 2002 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 75, 1263–1267 (2002)

Crystal- and Solution-Structure Characteristics of Ethylenediaminetetraacetatoaluminate(III) and Gallate(III)

Woo-Sik Jung,* Young Keun Chung,† Dong Mok Shin,† and Sun-Deuk Kim††

School of Chemical Engineering and Technology, College of Engineering, Yeungnam University,
Gyongsan 712-749, Korea

†School of Chemistry, College of Natural Sciences, Seoul National University,
San 56-1, Shillim-dong, Kwanak-gu, Seoul 151-742, Korea

††Department of Chemistry, Taegu University, Gyongsan 713-714, Korea

(Received November 9, 2001)

The structures of complex anions, $[Al(edta)]^-$ and $[Ga(edta)]^-$ (H_4edta = ethylenediaminetetraacetic acid), were investigated both in the solid state (X-ray crystallography) and in solution (^1H and ^{13}C NMR). Two complexes, $(NH_4)[Al(edta)]\cdot 2H_2O$ (**1**) and $(NH_4)[Ga(edta)]\cdot 2H_2O$ (**2**), are isostructural in the solid state. In both metal complexes, the central metal atoms are coordinated by six donor atoms (N_2O_4) in distorted octahedral coordination geometries in which two nitrogen atoms and two oxygen atoms of two acetate groups occupy the equatorial positions, and the axial positions are occupied by two oxygen atoms of two acetate groups. The ^1H and ^{13}C NMR spectra of **1** and **2** showed that acetate groups undergo rapid interchanges between the axial and equatorial positions in solution, its rate in D_2O being much faster than that in dimethyl sulfoxide(dmso)-d_6 for each complex, and its rate for **1** being slower than that for **2**. Based on the NMR spectra, the structures of complex anions $[Al(edta)]^-$ and $[Ga(edta)]^-$ in solution are concluded to be the same as those in the solid state.

Previous single-crystal X-ray crystallographic studies on metal ion (except for lanthanide ions) complexes of ethylenediaminetetraacetate anion (edta^{4-}) show that there are two main structural types of 6- and 7-coordinate complexes. The 6-coordinate complexes are further classified into three types, as follows. The first type (structure I) is that central metal ions are wrapped only by edta^{4-}, i.e., the donor atoms of which are four carboxylate oxygens atoms and two nitrogen atoms. The second one (structure II) is that one of four glycinate rings in the 6-coordinate complexes breaks open due to the occupation of unidentate ligands, leaving one acetate group uncoordinated.[1] The third one (structure III) is that one carboxylate is protonated, and therefore pendant to the central metal complex, with the vacated site being filled by a solvent molecule.[2] The structure of 7-coordinate complexes is a distorted monocapped trigonal prism or a pentagonal bipyramid. One of the complexes with the latter structure is $Li[Fe(edta)(OH_2)]\cdot 2H_2O$,[3] where a water molecule occupies a site in the pentagonal plane as the seventh ligand, together with the sexidentate edta^{4-}.

There always remains doubt regarding $[Al(edta)]^-$ as to whether the aforementioned structures established in the solid-state based on X-ray studies are the same as those in solution. A crystallographic study, in which the detailed geometric parameters were not described, of the solid $K[Al(edta)]\cdot 2H_2O$ was reported[4] and showed that the Al atom is coordinated only by the sexidentate edta^{4-}, and that there is no water molecule in its inner coordination sphere. On the other hand, in their studies concerning the molar heat capacities and volumes, Hovey and Tremaine[5] suggested that $[Al(edta)]^-$ in an aqueous solution exists as a dynamic equilibrium among the 7-coordinate complex with the same structure as $[Fe(edta)(OH_2)]^-$ [3] and 6-coordinate complexes with structures I and II. Nemes et al.[6] interpreted their kinetic data based on the formation of the $[Al(edta)F]^{2-}$ mixed ligand complex from the reaction between $[Al(edta)]^-$ and F^- or HF, assuming that one (or two) water molecule(s) is coordinated to $[Al(edta)]^-$.

The aim of this study was to establish whether or not the structure of $[Al(edta)]^-$ in solution is the same as that established in the solid state by an X-ray study. The crystal- and solution-structure characteristics of $(NH_4)[Al(edta)]\cdot 2H_2O$ (**1**) are described. In order to determine the solution structure, NMR spectroscopy was used because if the metal–ligand bonds in the coordination compound are long-lived compared to the NMR time scale, considerable information about the solution structure can be obtained.[7,8] The crystal- and solution-structure characteristics for **1** are compared with those for a gallium analogue of **1**. A crystal-structure study of $Na[Ga(edta)]\cdot 3H_2O$ showed that the Ga(III) ion is coordinated only by the sexidentate edta^{4-}.[9]

Experimental

Preparation of $(NH_4)[Al(edta)]\cdot 2H_2O$ (1). A slurry of freshly prepared $Al(OH)_3$ [obtained by the addition of 1 M aqueous ammonia to a solution of $Al(NO_3)_3\cdot 9H_2O$ (3.94 g, 10.5 mmol) in water (100 cm^3)] was treated with H_4edta (2.92 g, 10 mmol) in water (100 cm^3) and refluxed for 6 h. A clear solution obtained by filtering any unreacted H_4edta was treated with 1 M aqueous ammonia (10 mmol) and concentrated to 10 cm^3. Methanol was then

Table 1. Crystallographic Data and Experimental Details for **1** and **2**

	1	**2**
Empirical formula	$C_{10}H_{20}AlN_3O_{10}$	$C_{10}H_{20}GaN_3O_{10}$
Formula weight	369.27	412.01
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
Unit Cell dimensions		
a /Å	6.5518(1)	6.5840(1)
b /Å	10.137(1)	10.146(1)
c /Å	23.408(1)	23.402(1)
V /Å^3	1554.6(2)	1563.3(2)
Z	4	4
D_{calc}/g cm^{-3}	1.578	1.751
θ range /°	1.74 – 27.50	1.74 – 27.57
Crystal size /mm^3	0.5 × 0.6 × 1.0	0.5 × 0.4 × 1.0
Unique reflections	3586	3608
Goodness of fit on F^2	1.139	1.151
Final R indices [$I > 2\sigma(I)$]$^{a)}$	$R_1 = 0.0299$	$R_1 = 0.0450$
	$wR_2 = 0.0711$	$wR_2 = 0.1144$
R indices (all data)	$R_1 = 0.0457$	$R_1 = 0.0564$
	$wR_2 = 0.1024$	$wR_2 = 0.1314$

a) $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]]^{1/2}$

added with rigorous stirring at room temperature, and the resulting crude white crystals were filtered off and washed with methanol. Yield 3.18 g. Single crystals for X-ray crystallography were obtained by dissolving the crude crystals in water and evaporating the solvent slowly.

Preparation of $(NH_4)[Ga(edta)]\cdot 2H_2O$ (2). This complex and single crystals for X-ray crystallography were prepared by the same procedure as that described for **1**, except that $Ga(NO_3)_3\cdot 9H_2O$ was used instead of $Al(NO_3)_3\cdot 9H_2O$.

NMR Spectra Measurements. NMR spectra were recorded on Bruker DPX-300 (^{1}H, 300 MHz; ^{13}C, 75.48 MHz) and AMX-500 (^{1}H, 500 MHz) spectrometers. The values of the ^{1}H and ^{13}C chemical shifts in D_2O and dmso-d_6 were relative to sodium 2,2-dimethyl-2-silapentane-5-sulfonate in D_2O and to dmso-d_6 (2.49 ppm for ^{1}H, 39.70 ppm for ^{13}C), respectively.

X-ray Diffraction Studies. Single-crystal X-ray data were collected on an Enraf-Nonius CCD single-crystal X-ray diffractometer at 20 °C using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using SHELXS-97, and were refined against all F^2 data using SHELXL-97.[10] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms (HO1, HO2, HO3, HO4, HN1, HN2, HN3 and HN4) in **1** and **2** were found in a Fourier map and refined. The remaining hydrogen atoms were treated as idealized contributions. Crystal data and experimental details of the crystal structure determination are given in Table 1. The CIF data for two crystals are deposited as Document No. 75030 at the Office of the Editor of Bull. Chem. Soc. Jpn. Tables of the non-hydrogen atom coordinates and anisotropic thermal parameters, coordinates of the hydrogen atoms and bond lengths and angles have been deposited (Nos. CCDC 161170 and 161171 for **1** and **2**, respectively) at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

Results and Discussion

X-ray Crystal Structures. The crystal structures of **1** and **2** were isomorphous; an ORTEP drawing of **1** is depicted in Fig. 1. The stereochemistry and space group of **1** and **2** are the same as those of other sexidentate edta^{4-} complexes, such as $(NH_4)[Co(edta)]\cdot 2H_2O$[11] and $K[Mn(edta)]\cdot 2H_2O$.[12] As shown in Fig. 1, the coordination geometry around the metal atom is a distorted octahedron in which two nitrogen atoms and two oxygen atoms of the two acetate groups occupy the equatorial positions, and axial positions are occupied by two oxygen atoms of two acetate groups. Following the terminology of Hoard,[11] the less strained glycinate rings (N1– Al(Ga)–O1 and N2–Al(Ga)–O5) are called R and the more strained (N1–Al(Ga)–O3 and N2–Al(Ga)–O7) are called G. The five-membered ring containing the two nitrogen atoms, the Al(Ga) atom and the two methylene carbons is designated as E. Weakliem and

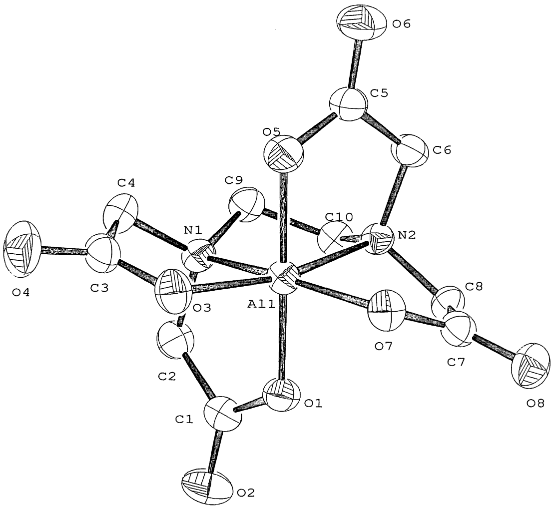

Fig. 1. Perspective ORTEP drawing of **1**. Thermal ellipsoids are drawn at the 50% probability level. The counter cation, two water molecules of crystallization and hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Bond Angles (°) for **1** and **2**

1		**2**	
Al–O(1)	1.877(2)	Ga–O(1)	1.971(2)
Al–O(3)	1.865(2)	Ga–O(3)	1.946(2)
Al–O(5)	1.882(2)	Ga–O(5)	1.972(2)
Al–O(7)	1.850(2)	Ga–O(7)	1.932(2)
Al–N(1)	2.072(2)	Ga–N(1)	2.109(2)
Al–N(2)	2.051(2)	Ga–N(2)	2.081(2)
O(1)–Al–O(3)	93.79(7)	O(1)–Ga–O(3)	95.53(13)
O(3)–Al–O(5)	87.60(7)	O(3)–Ga–O(5)	87.30(13)
O(1)–Al–O(5)	175.61(7)	O(1)–Ga–O(5)	176.68(12)
O(1)–Al–O(7)	87.99(7)	O(1)–Ga–O(7)	87.52(13)
N(1)–Al–O(1)	83.65(7)	N(1)–Ga–O(1)	83.47(12)
N(2)–Al–O(1)	94.04(7)	N(2)–Ga–O(1)	93.89(13)
N(1)–Al–O(3)	83.16(7)	N(1)–Ga–O(3)	82.84(12)
N(1)–Al–O(5)	92.39(7)	N(1)–Ga–O(5)	95.20(12)
N(2)–Al–O(5)	83.68(7)	N(2)–Ga–O(5)	82.97(13)
N(2)–Al–O(7)	83.30(7)	N(2)–Ga–O(7)	82.43(14)
N(1)–Al–N(2)	84.83(7)	N(1)–Ga–N(2)	85.42(13)

Hoard proposed that the sum of the angles of the five-membered chelate rings could be used as a measure of the strain in forming the chelate-metal ion bond.[11] The idealized angle sum for the E ring is 527.9°, while the glycinate rings with no strain would have an angle sum of 538.9°. The angle sums obtained from Table 2 in **1** (**2**) are as follows: E ring, 515.7° (514.4°); R ring for O1, N1 chelation, 538.2° (537.6°); R ring for O5, N2 chelation, 537.1° (538.5°); G ring for O3, N1 chelation, 526.8° (524.3°); G ring for O7, N2 chelation, 524.5° (526.6°). These values show that the angle sums in both complexes are very similar to each other, and that the G rings are more strained than the R rings. The magnitude of the geminal coupling constants of glycinate protons in the ^{1}H NMR spectra provides a valuable diagnostic for assigning the R and G rings (vide infra).[13]

The average Al(Ga)–N, Al(Ga)–O_G, and Al(Ga)–O_R distances are 2.062(2.095), 1.858(1.939), and 1.880(1.972) Å, respectively. Replacing the Al atom with the Ga atom causes the Ga–N, Ga–O_G and Ga–O_R bond distances to increase by 0.033, 0.081 and 0.092 Å, respectively. These differences for metal-oxygen bonds are almost the same as that of 0.08 Å between the effective ionic radii of six-coordinated Al^{3+} and Ga^{3+}.[14] The relatively small difference for the M–N bond distances indicates a stronger bonding of Ga–N than that of Al–N due to the higher affinity of (softer) Ga^{3+} for N donors.[15] The two metal–oxygen bond distances of the R rings are equivalent within the experimental error, while the two metal-oxygen bond distances of the G rings show a difference of 0.01 Å. The Al(Ga)–O bonds of the R rings are longer by ca. 0.02 Å (0.03 Å) than those of the G rings. The difference is contrary to that for $(NH_4)[Co(edta)]\cdot 2H_2O$,[11] where the average Co–O_R bond distance is shorter by 0.03 Å than the average Co–O_G bond distance.

The average Al–O and Al–N distances are very comparable to those found in $[Al(nta)(H_2O)_2]$ (H_3nta = nitrilotriacetic acid) (d_{av} = 1.881 Å for Al–O and d = 2.086 Å for Al–N).[16] The average Ga–O bond distance for **2** is similar to that for the complex $[Ga(Hedta)(OH_2)]$,[2] in which one of two oxygen donor atoms in the more strained G rings is protonated and freed from coordination. The G-ring opening leads to an increase in the Ga–N bond distance by 0.073 Å due to a release of the ring strain, while the other Ga–N bond distances for $[Ga(Hedta)(OH_2)]$ are longer by 0.016 Å than that for **2**. The difference in each Ga–N distance between **2** and $[Ga(Hedta)(OH_2)]$ is very close to that between **1** and [Al(Hedta)(dmso)],[17] the crystal structure of the latter complex being the same as that of $[Ga(Hedta)(OH_2)]$.

Considering that the effective ionic radius (0.620 Å) of Ga(III) (d^{10}) is very similar to that (0.645 Å) of high-spin Fe(III) (d^5) in six-coordinated complexes,[14] and that their charge distributions are spherically symmetric, it is interesting that the crystal structure of $[Ga(edta)]^-$ is not the same as that of the Fe(III) $edta^{4-}$ analogue, $[Fe(edta)(OH_2)]^-$.[3] We note that $[Ga(Hedta)(OH_2)]$ and $[Fe(Hedta)(OH_2)]$ are isostructural.[2]

The average of the C–O (ring oxygens) bond lengths for **1** and **2** is 1.29 Å, which is longer than the value of 1.23 Å for the external C=O distances. This is consistent with a decrease in the double-bond character of the C–O bond upon coordination of the ring oxygens to central metal ions, as shown in other $edta^{4-}$ complexes, such as $[Fe(edta)(OH_2)]^-$,[3] $[Co(edta)]^-$ [11] and $[Mn(edta)]^-$.[12]

^{13}C NMR Spectra. The structures of **1** and **2** in solution were studied by ^{1}H and ^{13}C NMR spectroscopy. The ^{13}C NMR spectra of **1** and **2** dissolved in D_2O showed three peaks at 56.00, 62.30 and 176.07 ppm for **1** and 56.05, 61.55 and 175.50 ppm for **2**, which are assigned to ethylenic, glycinate methylene and carboxylate carbons, respectively. The ^{13}C NMR spectra of **1** and **2** dissolved in dmso-d_6 are displayed in Fig. 2. In the spectrum of **1**, the peaks of glycinate methylene and carboxylate carbons are split into two peaks with almost the same intensities, while in the spectrum of **2** the carboxylate resonance is one and two glycinate resonances are broader than those of **1**. The spectrum pattern of Fig. 2(a) was also observed for $[Co(edta)]^-$ in D_2O,[1] indicating that the structure of $[Al(edta)]^-$ in dmso is consistent with that found in the solid state and the rate of interchange of acetate groups between axial and equatorial positions is slowed by dissolving **1** in dmso. It is noted that $[Co(edta)]^-$ in aqueous solution retains the same structure I as that in the solid state, and that Co(III) is inert in the ligand substitution reactions. For **2**, the interchange averages out two very close peaks of carboxylate carbons and broadens two relatively separated peaks of glycinate methylene carbons. Based on this NMR evidence, it is tenable to suggest that the crystal structure of $[Ga(edta)]^-$ is conserved in solution, as in the case for $[Al(edta)]^-$.

The spectrum patterns of $edta^{4-}$ complexes are determined by the lability of individual metal-ligand bonds.[1,7,8] The fact that only three peaks for **1** and **2** in D_2O were observed suggests that acetate groups undergo a rapid interchange between the axial and equatorial positions, as reported for labile complexes, such as $[Pb(edta)]^{2-}$, $[Zn(edta)]^{2-}$, $[Cd(edta)]^{2-}$ and $[Hg(edta)]^{2-}$,[1] on the NMR time scale. A comparison between Figs. 2(a) and (b) reveals that the interchange of the acetate groups is slower for **1** than for **2**. This is easily explained by the difference in the lability of the Al^{3+} and Ga^{3+} ions, with the

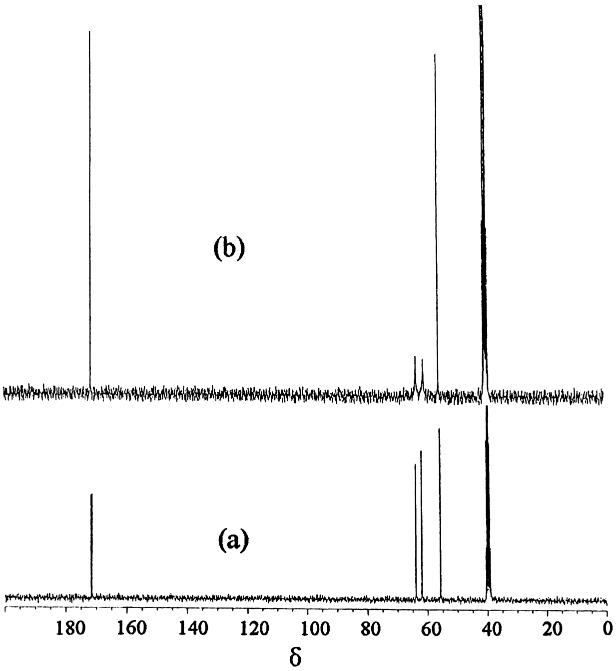

Fig. 2. ^{13}C NMR spectra of **1**(a) and **2**(b) in dmso-d_6.

first-order water exchange rate constants for $[Al(OH_2)_6]^{3+}$ and $[Ga(OH_2)_6]^{3+}$ being 1.3[18] and 4.0×10^2 s^{-1} at 298 K,[19] respectively.

The interchange of the acetate groups between the axial and equatorial positions in $[Al(edta)]^-$ and $[Ga(edta)]^-$ could take place by two mechanisms, i.e., bond rupture and twist mechanisms.[8] Although our limited experimental results provide no definitive basis for distinguishing between the mechanisms, two lines of evidence can cited in support of a bond-rupture mechanism. First, if a bond-rupture mechanism is operative, the interchange is expected to be much faster in D_2O than in dmso-d_6 because, in general, the rate of the reaction separating oppositely charged ions increases with the dielectric constant of the medium. Also, the interchange by a twist mechanism without the rupture of any metal–ligand bonds should show a slight solvent dependence on its rate. Second, the interchange rate is expected to decrease along with an increase in the pH, and the peak splitting would be observed for $[Al(edta)]^-$ at a high pH.[1]

Figure 3 shows the ^{13}C NMR spectrum of a mixture of $[Al(edta)^-] = 0.30$ M and $[NaF] = 0.12$ M in D_2O, in which the main chemical species would be $[Al(edta)]^-$ and $[Al(edta)F]^{2-}$ with the mole ratio being 3:2 because of the equilibrium constant for the reaction $[Al(edta)]^- + F^- = [Al(edta)F]^{2-}$ is $10^{4.8}$ M^{-1}.[20] The spectrum given in Fig. 3 is, therefore, considered to be a superposition of the spectra of $[Al(edta)]^-$ and $[Al(edta)F]^{2-}$. The structure of $[Al(edta)F]^{2-}$ is expected to be the same as that (structure II) of $[Co(edta)X]^{2-}$, where one of four glycinate rings breaks open because of the occupation of the X^- ion, leaving one acetate group uncoordinated (since the equatorial G rings are more strained than the axial R rings, they break open more easily in the presence of the F^- ion).[1] However, the number of peaks pertaining to $[Al(edta)F]^{2-}$ is seven, which is less by three than for $[Co(edta)X]^{2-}$ because $[Al(edta)F]^{2-}$ is not so stereochemically rigid as $[Co(edta)X]^{2-}$. Each peak was tentatively assigned as follows: 60.40 and 176.80 ppm, uncoordinated glycinate methylene and carboxylate carbons, respectively; 55.53 and 56.00 ppm, ethylenic carbons; 62.30 and 62.63 ppm, coordinated glycinate methylene carbons; 176.07 ppm, coordinated carboxylate carbons. The difference in the chemical shift between the uncoordinated and coordinated acetate carbons is relatively larger for $[Co(edta)X]^{2-}$ than for $[Al(edta)F]^{2-}$ due to the temperature-independent paramagnetic contribution of the Co(III) ion.

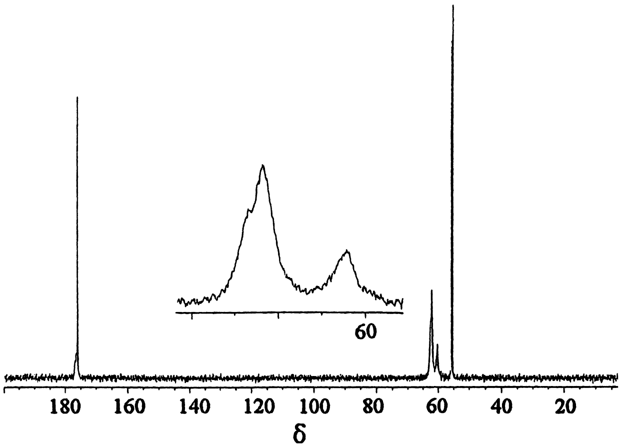

Fig. 3. ^{13}C NMR spectrum of a mixture of $[Al(edta)^-] = 0.30$ M and $[NaF] = 0.12$ M in D_2O.

If there are one or more water molecules in the inner coordination sphere of $[Al(edta)]^-$,[5] the water molecule(s) will be substituted by dmso or F^- ion without a change in the structure. The observation that the ^{13}C NMR spectrum of **1** dissolved in dmso-d_6 is very different from that of $[Al(edta)F]^{2-}$ means that there is no water molecule in the inner coordination sphere of $[Al(edta)]^-$. This conclusion is supported by preliminary kinetic studies concerning the substitution reaction between the $[Co(OH_2)_6]^{2+}$ ion and $[Al(edta)]^-$ in aqueous solution. The kinetic results obtained by spectrophotometry showed that the rate is accelerated by the addition of F^-. This is attributed to the formation of the $[Al(edta)F]^{2-}$ ion with an uncoordinated acetate group, which is easily coordinated to a hydrated Co(II) ion. If $[Al(edta)]^-$ is an 7-coordinate complex with edta^{4-} being sexidentate, there would be little difference in the substitution reaction between $[Al(edta)]^-$ and $[Al(edta)F]^{2-}$.

^{1}H NMR Spectra. The ^{1}H NMR spectra of **1** and **2** dissolved in D_2O showed two peaks, including one broad singlet and one quartet peak. The linewidth of the singlet peak assigned to ethylenic protons is broader for **1** (66 Hz) than for **2** (14 Hz) because the Al^{3+} ion is less labile than the Ga^{3+} ion. One quartet peak is assigned to glycinate methylene protons. Because the bonded nitrogen is asymmetric, the methylene protons are nonequivalent, giving rise to an AB-type spin-spin splitting pattern.[7] The geminal coupling constants for two complexes were determined to be −17.8 Hz. No peak corresponding to methylene protons on an uncoordinated acetate was observed. If an uncoordinated acetate exists, its AB pat-

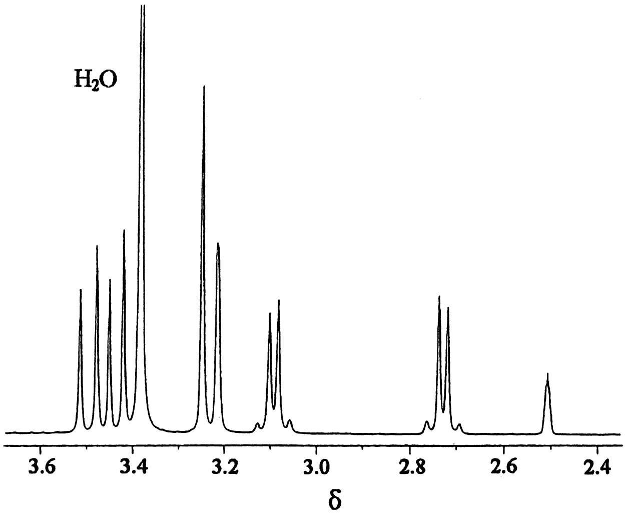

Fig. 4. 500 MHz ^{1}H NMR spectrum of **1** in dmso-d_6.

tern will be nearly collapsed due to a very small chemical shift difference between the protons.

Figure 4 shows the 500 MHz ^{1}H NMR spectrum of **1** dissolved in dmso-d_6, where the interchange of acetate groups between axial and equatorial positions is much slower than that in D_2O. The spectrum pattern is very similar to that[21] of $[Co(edta)]^-$ in D_2O, in that two AB-system quartets and one AA′BB′-system near-quartet are observed. This leads to the conclusion that the structure of $[Al(edta)]^-$ in solution is the same as that of $[Co(edta)]^-$ in solution. Two near-quartet peaks centered at 2.72 and 3.08 ppm with the same intensity arise from the protons on the ethylenic backbone of the ligand $edta^{4-}$. Two quartets (δ 3.22, 3.25, 3.42, 3.45; δ 3.22, 3.25, 3.48, 3.52) centered at 3.33 and 3.36 ppm, each having the geminal coupling constants of -15.3 and -18.2 Hz, are assigned to glycinate protons in the G and R rings, respectively. Note that the peaks at 3.22 and 3.25 ppm are not resolved. The assignments of the two quartets are based on the magnitudes of the geminal coupling constants. The coupling constants of the glycinate protons are more negative in the R rings than in the G rings because the G rings are more strained than the R rings,[6] as evidenced in the above-mentioned crystal structure. In the spectrum of **2** dissolved in dmso-d_6, the splitting patterns are nearly collapsed and the peaks are broadened because the interchange of acetate groups between the axial and equatorial positions is faster for the Ga^{3+} ion than for the Al^{3+} ion.

Based on the NMR evidence, it is most likely concluded that the crystal structures of the complex anions $[Al(edta)]^-$ and $[Ga(edta)]^-$ remain intact in solution. The possibility is ruled out that the six-coordinate complex anions with the ligand sexidendate $edta^{4-}$ co-exist in rapid equilibrium with the 7-coordinate species containing one water molecule and the 6-coordinate species with an uncoordinated acetate group.

This research was supported by grant No. R02-2001-00841 from the Basic Research Program of the Korea Science & Engineering Foundation.

References

1 O. W. Howarth, P. Moore, and N. Winterton, *J. Chem. Soc., Dalton Trans.*, **1974**, 2271.

2 C. H. L. Kennard, *Inorg. Chim. Acta*, **1**, 347 (1967).

3 M. D. Lind, J. L. Hoard, M. J. Hamor, and T. A. Hamor, *Inorg. Chem.*, **3**, 34 (1964).

4 T. N. Polynova, N. P. Bel′skaya, D. Tyurk de Garciya Banus, M. A. Porai-Koshitsn, and L. I. Martynenko, *Z. Struct. Khim.*, **11**, 164 (1970).

5 J. K. Hovey and P. Tremaine, *J. Phys. Chem.*, **89**, 5541 (1985).

6 J. Nemes, I. Tóth, and L. Zékány, *J. Chem. Soc., Dalton Trans.*, **1998**, 2707.

7 R. J. Day and C. N. Reilley, *Anal. Chem.*, **36**, 1073 (1964).

8 R. J. Day and C. N. Reilley, *Anal. Chem.*, **37**, 1326 (1965).

9 K. Nakamura, T. Kurisaki, H. Wakita, and T. Yamaguchi, *Acta Crystallogr., Sect. C*, **52**, 573 (1996).

10 G. M. Sheldrick, "SHELX-97, Programs for Crystal Structure Analysis," University of Göttigen, Germany (1997).

11 A. Weakliem and J. L. Hoard, *J. Am. Chem. Soc.*, **81**, 549 (1959).

12 J. Stein, J. P. Fackler, Jr., G. J. McClune, J. A. Fee, and L. T. Chan, *Inorg. Chem.*, **18**, 3511 (1979).

13 J. L. Sudmeier, A. J. Senzen, and G. Blackmer, *Inorg. Chem.*, **10**, 90 (1971).

14 R. D. Shannon, *Acta Crystallogr., Sect. A*, **32**, 751 (1976).

15 R. G. Pearson, *Inorg. Chem.*, **27**, 734 (1988).

16 G. C. Valle, G. G. Bombi, B. Corain, M. Favarato, and P. Zatta, *J. Chem. Soc., Dalton Trans.*, **1989**, 1513.

17 Crystal structural results have been deposited (No. CCDC 161172) at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

18 D. Hugi-Cleary, L. Helm, and A. E. Merbach, *Helv. Chim. Acta*, **68**, 545 (1985).

19 D. Hugi-Cleary, L. Helm, and A. E. Merbach, *J. Am. Chem. Soc.*, **109**, 4444 (1987).

20 I. Tóth, L. Zékány, and V. Veksin, *Polyhedron*, **8**, 2057 (1989).

21 O. W. Howarth, *Polyhedron*, **2**, 853 (1983).