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Raman Study of the Coordination Structure of a Rare Earth−Acetate Complex in Water

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The Raman spectra of aqueous $LnCl_3 \cdot 20H_2O \cdot CH_3COOLi$ ($LnCl_3$, rare earth chloride) solutions have been measured in the liquid state. The change of the Raman symmetric $Ln^{3+}-OH_2$ stretching band (ν_w) showed that the decrease in the ionic radius of rare earth (Ln^{3+}) ions induces a change in coordination number of the Ln^{3+} ion. The two peaks at 946 and 958 cm^{-1} of the C−C stretching band (ν_{CC}) of the acetate ion are assigned to the bidentate ligand and the polymeric chain structure, respectively. The coordination structure of the acetate ion to Ln^{3+} ion prefers the bidentate ligand to the polymeric chain structure throughout the rare earth series. The fraction of the bidentate ligand increases with decreasing ionic radius of the Ln^{3+} ion. On the basis of the analyses of the ν_w and ν_{CC} bands, the change in the coordination number of the Ln^{3+} ion is mainly due to the structural change (from the polymeric chain structure to the bidentate ligand) of the Ln^{3+}−acetate complex rather than a elimination of one water molecule. Our results show that the Ln^{3+} ions tend to form the bidentate ligand rather than the divalent (M^{2+}) ions.

1. Introduction

There have been several studies of aqueous rare earth electrolyte solutions.[1] Many experimental techniques, such as X-ray diffraction,[2−4] Raman spectroscopy,[5] and thermodynamics,[6−9] have been applied to investigate the complex formation of rare earth (Ln^{3+}) ions in water.

Many thermodynamic and transport properties of aqueous rare earth electrolyte solutions show irregularities when plotted against the ionic radius,[7−9] although the ionic radius of Ln^{3+} ion decreases smoothly from lanthanum (La^{3+}) to lutetium (Lu^{3+}) ions because of lanthanide contraction. It is known that the coordination number of Ln^{3+} ions in glassy aqueous rare earth chloride ($LnCl_3$) solutions changes from 9 for the light Ln^{3+} ions ($La^{3+}-Sm^{3+}$) to 8 for the heavy Ln^{3+} ions ($Tb^{3+}-Ln^{3+}$).[5,10−12] A similar change in the coordination number for the Ln^{3+} ions in the middle region ($Gd^{3+}-Ho^{3+}$ or Er^{3+}) of the rare earth series has been observed in alcohol $LnCl_3$ solutions.[13,14] Therefore, it would also be interesting to determine whether the coordination number of Ln^{3+} ions in aqueous carboxylic acid solutions changes.

Another interesting topic is that the study of the coordination behavior of the carboxylate ($RCOO^-$, R = alkyl chain) ion with Ln^{3+} ion is important for understanding the additive effect of Ln^{3+} ions on the helix−coil transition of poly-L-glutamic acid (PLGA), which is a model polypeptide of the fold−unfold equilibrium of a protein. It is widely accepted that the addition of divalent cations (M^{2+} ions) such as Mg^{2+} and Ca^{2+} ions to PLGA enhances the structural stability of the α-helix by chelate formation between the COO^- group of the side chain and the M^{2+} ions.[15,16] There are three typical representative structures of the metal cation (M)−COO^- complexes:[17−20] the monodentate, bidentate, and bridging bidentate ligands (Figure 1). It might be interesting to investigate the additive effect of Ln^{3+} ions on the structural stability of the α-helix of PLGA, because the ionic radii of Ln^{3+} ions are close to those of Mg^{2+} and Ca^{2+} ions. There are three typical representative strucutres of the metal cation (M)−COO^- complexes:[17−20] the monodentate, bidentate, and bridging bidentate ligands (Figure 1).

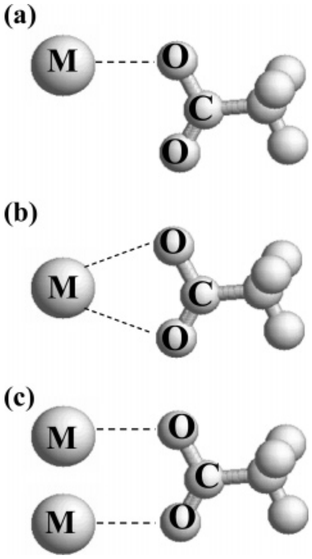

Figure 1. Three typical structures of the metal cation (M)−acetate ion (CH_3COO^-) complexes: (a) monodentate ligand, (b) bidentate ligand, and (c) bridging bidentate ligand.

The study on the coordination structure of the $RCOO^-$ ion such as an acetate ion to a Ln^{3+} ion was reported by Garza et al.[21] The result of ultrasonic absorption by Garza et al.[21] suggested that the acetate ion forms a bidentate ligand with the Ln^{3+} ion in water. However, there have been no other detailed studies on the coordination structure of the acetate ion with Ln^{3+} ion; the study by Garza et al.[21] is insufficient for the elucidation of the coordination behavior of the acetate ion.

In this study, we have measured the Raman symmetric Ln^{3+}−OH_2 stretching and C−C stretching spectra of $LnCl_3 \cdot 20H_2O \cdot CH_3COOLi$ and compared the results with those of the aqueous $LnCl_3$ and $MgCl_2$ solutions. There are some reasons that we employed $LnCl_3 \cdot 20H_2O \cdot CH_3COOLi$ solutions as the reagents. First, as the solubility of rare earth acetates is not too high [at most $Ln(CH_3COO)_3 \cdot 200-250H_2O$], the Raman $Ln^{3+}-OH_2$ stretching band, which is a measure of the coordination number change of a Ln^{3+} ion, is not observed in the aqueous

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$Ln(CH_3COO)_3$ solutions. The information of the coordination number change of Ln^{3+} ions in glassy rare earth chloride solutions ($LnCl_3{\cdot}20H_2O$; in this system, Cl^- ion does not coordinate to Ln^{3+} ion) is available in the literature.[5] Additionally, a metal (Ln^{3+} ion) to ligand (CH_3COO^- ion) ratio of 1:1 might be better than 1:3 to simply identify the coordination behavior of the acetate ion with a Ln^{3+} ion, because the acetate ion in aqueous $Ln(CH_3COO)_3$ solutions could induce more complex coordination structures. Therefore, we have investigated the $LnCl_3{\cdot}20H_2O{\cdot}CH_3COOLi$ solutions to study the coordination structure of rare earth−acetate complex in water. We show that the coordination structure of the acetate ion to Ln^{3+} ion prefers the bidentate ligand to the polymeric chain structure throughout the rare earth series.

2. Materials and Methods

Rare earth chlorides ($LnCl_3$; $Ln^{3+} = La^{3+} - Lu^{3+}$) were obtained from Soekawa Chemical Co. Lithium acetate (CH_3COOLi) and magnesium chloride ($MgCl_2$) were obtained from Wako Junyaku Industry Co. Ltd. All sample solutions ($LnCl_3{\cdot}20H_2O$, $LnCl_3{\cdot}20H_2O{\cdot}CH_3COOLi$, and $MgCl_2{\cdot}20H_2O{\cdot}CH_3COOLi$) were prepared by dissolving the required amounts of $LnCl_3$ or $MgCl_2$ and CH_3COOLi in water.

Raman spectra were measured by a Jasco NR-1800 Raman spectrophotometer equipped with a single monochromator and a charge-coupled device (CCD) detector. The exposure time of each run and spectral resolution were 300 s and 4.5 cm^{-1}, respectively. The 514.5 nm line from Lexel Ar^+ ion laser was used as an exacting source with a power of 350 mW. The liquid samples were measured at room temperature. The obtained spectra were fitted with the Gaussian−Lorentzian mixing functions using the GRAMS/386 software (Galactic Ind. Co. Ltd.) to analyze the $Ln^{3+}{-}OH_2$ and C−C stretching bands.

3. Results and Discussion

Figure 2a shows the Raman spectra in the region from 250 to 500 cm^{-1} of $LnCl_3{\cdot}20H_2O{\cdot}CH_3COOLi$ as a function of Ln^{3+} ion. It is well-known that when the interaction between the metal cation (M) and the coordinated water molecules are strong enough, a Raman band due to the symmetric $M{-}OH_2$ stretching vibration (ν_w) is observed in the low-frequency region from 300 to 550 cm^{-1}.[5,22−26] Basically, the Raman ν_w band of aqueous $LnCl_3$ solution in the liquid state is weaker than that in the glassy state because of the overwhelmingly strong Raman scattering wing.[5] The clear characterization of the ν_w band is possible when the solution is vitrificated. A Raman spectrophotometer equipped with a high performance CCD detector, however, enabled us to observe the weak ν_w band of $LnCl_3{\cdot}20H_2O$ and $LnCl_3{\cdot}20H_2O{\cdot}CH_3COOLi$ in the liquid state. According to the previous Raman study,[5] the Raman symmetric $La^{3+}{-}OH_2$ stretching band (ν_w) in the aqueous $LaCl_3$ solution is observed in the region from 330 to 385 cm^{-1} in the liquid and glassy states. On the other hand, the Raman symmetric M−O stretching band of the M−anion complex such as CH_3COO^-, NO_3^-, and ClO_4^- in aqueous solution is observed in the region from 180 to 230 cm^{-1}.[22,27,28] Unfortunately, in this study, the Raman symmetric $Ln^{3+}{-}O$ stretching band of the Ln^{3+}−acetate complex could not be observed in this region due to the strong Rayleigh scattering wing. We applied the Raman ν_w band for the investigation of the coordination behavior of Ln^{3+} ion in $LnCl_3{\cdot}20H_2O{\cdot}CH_3COOLi$.

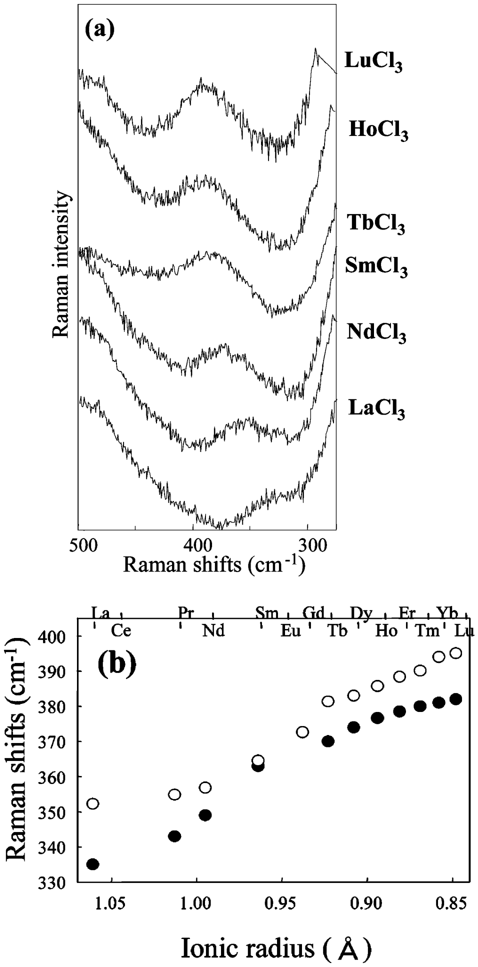

Figure 2. (a) Typical Raman $Ln^{3+}{-}OH_2$ stretching (ν_w) spectra of aqueous $LnCl_3{\cdot}CH_3COOLi$ solutions as a function of Ln^{3+} ion and (b) the ν_w frequency variations in the $LnCl_3{\cdot}20H_2O$ and $LnCl_3{\cdot}20H_2O{\cdot}CH_3COOLi$ as a function of ionic radius (r) of Ln^{3+} ion. The open and closed circles represent the $LnCl_3{\cdot}20H_2O$ and $LnCl_3{\cdot}20H_2O{\cdot}CH_3COOLi$, respectively.

Figure 2b compares the ν_w frequency variations of $LnCl_3{\cdot}20H_2O$ and $LnCl_3{\cdot}20H_2O{\cdot}CH_3COOLi$ in the liquid state as a function of ionic radius of Ln^{3+} ion. A remarkable point in Figure 2b is that the S-shaped behavior of the ν_w frequencies in both solutions is shown, and these frequencies rapidly increase from Nd^{3+} to Tb^{3+} ions for $LnCl_3{\cdot}20H_2O$ by about 25 cm^{-1} and from Nd^{3+} to Sm^{3+} ions for $LnCl_3{\cdot}20H_2O{\cdot}CH_3COOLi$ by 14 cm^{-1}, respectively. On the whole, the value of the ν_w frequency of $LnCl_3{\cdot}20H_2O{\cdot}CH_3COOLi$ is lower than that of $LnCl_3{\cdot}20H_2O$.

It was concluded that the S-shaped behavior of the Raman frequency shift[15,16] and thermodynamic properties[7,29−32] throughout the rare earth series are caused by the change in the coordination number of the Ln^{3+} ion. Kanno et al.[5,10,12] reported that the ν_w frequency of the $LnCl_3{\cdot}20H_2O$ solutions in the glassy state shifts to a higher frequency from La^{3+} to Lu^{3+} ions, and the two ν_w peaks at 369 and 394 cm^{-1} are observed in the middle region (Eu^{3+} and Gd^{3+}). The two peaks at 369 and 394 cm^{-1} are assigned to the nine- and eight-coordination structures of the $[Ln(H_2O)_n]^{3+}$ complex ($n = 9{-}8$), respectively. The difference in the ν_w frequencies (25 cm^{-1}) corresponds to the elimination of a water molecule from $[Ln(H_2O)_9]^{3+}$ to $[Ln(H_2O)_8]^{3+}$ complexes. Importantly, the observed ν_w frequency shift between Nd^{3+} and Tb^{3+} ions for $LnCl_3{\cdot}20H_2O$ in the liquid state is 25 cm^{-1}, which is almost equal to that in the glassy state. This means that the coordination number of Ln^{3+} ion for $LnCl_3{\cdot}20H_2O$ in the liquid state might change from nine to eight

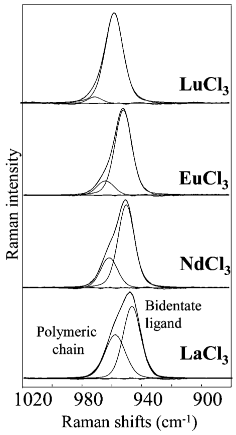

Figure 3. Typical Raman C−C stretching (ν_{CC}) spectra of the acetate ion in the aqueous $LnCl_3 \cdot CH_3COOLi$ solutions as a function of Ln^{3+} ion.

with decreasing ionic radius of the Ln^{3+} ion. On the other hand, the observed ν_w frequency shift between Nd^{3+} and Sm^{3+} ions in $LnCl_3 \cdot 20H_2O \cdot CH_3COOLi$ is 14 cm^{-1}, which is smaller than that in $LnCl_3 \cdot 20H_2O$. We suppose that the change in the coordination number of the Ln^{3+} ion may arise from the change in the coordinate structure of the acetate ion rather than the elimination of a water molecule as describe below.

Thus, we examined the coordination behavior of the acetate ion. Figure 3 shows the Raman C−C stretching (ν_{CC}) spectra of the acetate ion across the rare earth series. The two peaks at 946 and 958 cm^{-1} were determined by the second derivative of the original spectra. According to recent Raman studies of dilute aqueous acetate salt solutions such as $(CH_3COO)_2Mg$ and $(CH_3COO)_2Cu$,[33−36] the peak at around 945 cm^{-1} is assigned to the bidentate ligand. The observed peak at 946 cm^{-1} in aqueous $LnCl_3 \cdot CH_3COOLi$ solutions appeared in the same peak position as the bidentate ligand of dilute aqueous acetate salt solutions.[33−36] Therefore, we assigned the peak at 946 cm^{-1} to the bidentate ligand.

Recently, Wang et al.[35] revealed that the relative concentration of the polymeric chain structure, which constructs the bridging bidentate ligand of aqueous $(CH_3COO)_2Mg$ solution, increases with increasing salt concentration. The observed peak intensity at 958 cm^{-1} in aqueous $LnCl_3 \cdot CH_3COOLi$ solutions increases with increasing acetate ion concentration and that at 946 cm^{-1}, which is assigned to the bidentate ligand, decreases (data not shown). This result is qualitatively consistent with the salt concentration dependence of the polymeric chain structure of aqueous $(CH_3COO)_2Mg$ solutions. Therefore, the observed peak at 958 cm^{-1} in aqueous $LnCl_3 \cdot CH_3COOLi$ solutions might relate to a polymeric chain structure.

Next, we consider the polymeric chain structure of aqueous $LnCl_3 \cdot CH_3COOLi$ solutions. Ribot et al.[37] reported that the coordination state of $Ln(CH_3COO)_3 \cdot nH_2O$ ($n = 1-4$) in the crystal state takes a bridging complex and polymeric structure. Meyer determined the chain structure of $[Sm(CH_3COO)(H_2O)_6]Cl_3(H_2O)$, which takes an eight-coordinated structure, in the crystal state.[38] The chain structure of $[Sm(CH_3COO)(H_2O)_6]Cl_3(H_2O)$ consists of bidentate and bridging bidentate ligands. The polymeric structure suggested by Ribot et al.[37] may be close to the chain structure of $[Sm(CH_3COO)(H_2O)_6]Cl_3(H_2O)$. On the basis of the results of Ribot et al.[37] and Meyer,[38] we suggest that the polymeric chain structure of the acetate ion in aqueous $LnCl_3 \cdot CH_3COOLi$ solutions is as shown in Figure 4.

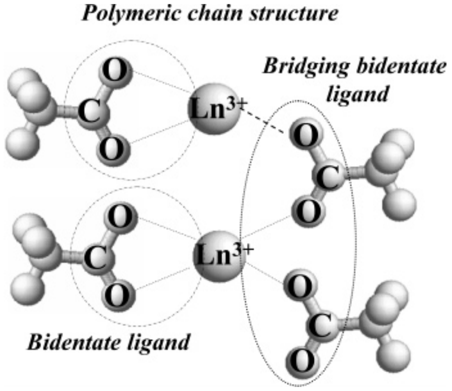

Figure 4. Simple scheme of the polymeric chain structure of the acetate ion to the Ln^{3+} ion in the aqueous $LnCl_3 \cdot CH_3COOLi$ solutions. The water molecules and chloride ions are not represented.

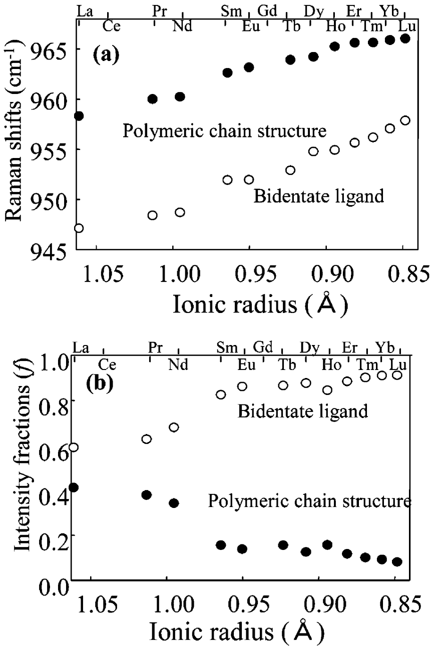

Figure 5. (a) ν_{CC} frequency variations and (b) the intensity fractions of the bidentate ligand and polymeric chain structure of the ν_{CC} band of the acetate ion as a function of ionic radius (r) of Ln^{3+} ion. The open and closed circles represent the bidentate ligand and polymeric chain structure, respectively.

To be certain of the above speculation, we performed the ν_{CC} frequency calculations of the bidentate ligand and polymeric chain structure of the La^{3+}−acetate complex using density functional theory (DFT) at the B3LYP/6-311++G(d,p) level.[39] The peaks at 982 cm^{-1} for the bidentate ligand and at 996 cm^{-1} for the polymeric chain structure were determined by this calculation. It is important to note that the observed frequency at 958 cm^{-1} for the polymeric chain structure is higher than that at 945 cm^{-1} for the bidentate ligand. The difference in the observed frequencies between the polymeric chain structure and the bidentate ligand is almost the same as that in the calculated frequencies. The calculated result is qualitatively consistent with the experimental result. Therefore, the assignment of the observed peak at 958 cm^{-1} to a polymeric chain structure is probably correct, although the length of the polymeric chain structure in the present study is unclear. We applied this assignment to the following discussion.

Next, we discuss the coordination structure of the acetate ion with Ln^{3+} ion. Figure 5a shows the ν_{CC} frequency variations of the bidentate ligand and polymeric chain structure across the rare earth series. On the whole, the ν_{CC} frequencies of the bidentate ligand and polymeric chain structure shift to a higher frequency with the decreasing ionic radius of Ln^{3+} ion. When the intermolecular electrostatic interaction between the Ln^{3+} and acetate ions becomes stronger, the force constant of the C−C bond of the acetate ion weakens and the ν_{CC} frequency shifts to a higher frequency. The slope of the ν_{CC} frequency of the bidentate ligand against the ionic radius of Ln^{3+} ion in Figure 5a is larger than that of the polymeric chain structure. This means that the intermolecular electrostatic interaction between the Ln^{3+}−bidentate ligands becomes stronger than that between the Ln^{3+}−polymeric chain structures with a decreasing ionic radius of Ln^{3+} ion.

Another remarkable point in Figure 5a is that the ν_{CC} frequencies of the bidentate ligand and polymeric chain structure rapidly increase from Nd^{3+} to Sm^{3+} ions; this is consistent with the results of the ν_w frequency change, as shown in Figure 2b. Thus, we suppose that the change in the coordination number of the Ln^{3+} ion has a close relationship with the change in the coordination behavior of the acetate ion.

To ensure the relation between the change in the coordination number of Ln^{3+} ion and the change of the coordination behavior of acetate ion, using the same procedure in the previous studies,[40,41] we estimated the intensity fractions (f) of the bidentate ligand ($f_{\text{bidentate}}$) and polymeric chain structure ($f_{\text{polymeric}}$) from the equations

$$f_{\text{bidentate}} = \frac{I_{\text{bidentate}}}{I_{\text{bidentate}} + I_{\text{polymeric}}}$$

$$f_{\text{polymeric}} = \frac{I_{\text{polymeric}}}{I_{\text{bidentate}} + I_{\text{polymeric}}}$$

where $I_{\text{bidentate}}$ and $I_{\text{polymeric}}$ represent the relative Raman intensities of the bidentate ligand and polymeric chain structure, respectively. Figure 5b shows the changes in $f_{\text{bidentate}}$ and $f_{\text{polymeric}}$ as a function of the ionic radius of Ln^{3+} ion. It is evident that $f_{\text{bidentate}}$ is dominant throughout the rare earth series. The value of $f_{\text{bidentate}}$ increases with decreasing ionic radius of Ln^{3+} ion and that of $f_{\text{polymeric}}$ decreases. Accordingly, our results show that the heavy Ln^{3+} ion prefers the bidentate ligand to the polymeric chain structure. As the ionic radius of Ln^{3+} ion decreases due to lanthanide contraction, it is highly possible that the change in the coordination structure of the acetate ion to Ln^{3+} ion is dominated by the size of Ln^{3+} ion.

Raman spectroscopy does not give a definite picture of the total coordination number around Ln^{3+} ions in the $LnCl_3 \cdot 20H_2O \cdot CH_3COOLi$. However, a plausible picture might be extracted from the present and available experimental data. As seen in Figure 2b, the value of ν_w frequency of $LnCl_3 \cdot 20H_2O \cdot CH_3COOLi$ is generally lower than about 20 cm^{-1} that of the corresponding $LnCl_3 \cdot 20H_2O$. From the empirical trend,[5,12,25] the formation of higher complex results in the decrease of the symmetric $M{-}OH_2$ stretching frequency. Therefore, the straightforward conclusion of this result is that it may arise from the difference in the numbers of coordinated water molecules to a Ln^{3+} ion between $LnCl_3 \cdot 20H_2O \cdot CH_3COOLi$ and $LnCl_3 \cdot 20H_2O$. However, there is another possibility that a negative deviation of the ν_w band for the acetate solution from that for the corresponding chloride solution arises from the matching between the Ln^{3+} ion and its coordination sphere when one acetate ion constitutes a part of the coordination sphere. If the matching is not so better, the $Ln^{3+}{-}OH_2$ interaction becomes weaker, resulting in the lower ν_w frequency for the acetate solution than that for the corresponding chloride solution. It is, however, difficult to say whether it is the case.

On the basis of the results of the ν_w and ν_{CC} frequencies and intensity fractions (f), we can conclude the following. (i) The coordination number of the Ln^{3+} ion should change and decrease by one (probably from nine to eight). (ii) The change in the coordination number of Ln^{3+} ion across the rare earth series is mainly due to the coordinated structural change (from the polymeric chain structure to the bidentate ligand) of the acetate ion rather than the elimination of one water molecule.

Finally, we discuss the difference in the coordination structures between divalent metal ion−acetate and rare earth−acetate complexes. As a candidate for this, we quote the Mg^{2+} and Tm^{3+} ions, because the ionic radius of the Mg^{2+} ion (0.860 Å)[42] is almost the same value as that of the Tm^{3+} ion (0.858 Å). The ν_{CC} frequencies of the bidentate ligand and the polymeric chain structure of the acetate ion in aqueous $MgCl_2$ solution (947 cm^{-1} for the bidentate ligand and 954 cm^{-1} for the polymeric chain structure) are lower than those in aqueous $TmCl_3$ solution (956 cm^{-1} for the bidentate ligand and 965 cm^{-1} for the polymeric chain structure). The values of $f_{\text{bidentate}}$ and $f_{\text{polymeric}}$ in aqueous $MgCl_2$ solution are 0.4 and 0.6, respectively. The situation reverses in aqueous $TmCl_3$ solution ($f_{\text{bidentate}}$:$f_{\text{polymeric}}$ = 0.9:0.1). These results clearly show that the intermolecular electrostatic interaction between the Tm^{3+} and the acetate ions is stronger than that between the Mg^{2+} and the acetate ions and that the Tm^{3+} ion tends to form the bidentate ligand rather than the Mg^{2+} ion.

4. Conclusions

The Raman $Ln^{3+}{-}OH_2$ (ν_w) and C−C stretching (ν_{CC}) spectra of the acetate ion in aqueous $LnCl_3 \cdot CH_3COOLi$ solutions have been measured as a function of ionic radius of Ln^{3+} ion. We discussed the change in the coordination structure of the acetate ion to Ln^{3+} ion. On the basis of the analyses of ν_w and ν_{CC} bands, the lanthanide contraction induces the change in the coordination number of the Ln^{3+} ion followed by the change in the coordination structure of the Ln^{3+}−acetate complex. The coordination structure of the acetate complex prefers the bidentate ligand to the polymeric chain structure.

On the basis of the results of the aqueous $MgCl_2$ and $TmCl_3$ solutions, the Ln^{3+} ions tend to form the bidentate ligand rather than the divalent (M^{2+}) ions. For the studies of the metal ions including Ln^{3+} ions binding to the active site in proteins, it is important to reveal the interaction and coordination structure between the metal ions and the COO^- groups of organic compounds such as acetate ion. More studies on the additive effect of Ln^{3+} ions on the structural stability of oligopeptides, including charged amino acid residues such as those of Asp and Glu, will help us to understand the additive effect of Ln^{3+} ions on the structural stability of proteins.

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