Interactions Between Hydrated Cerium(III) Cations and Carboxylates in an Aqueous Solution: Anomalously Strong Complex Formation with Diglycolate, Suggesting a Chelate Effect

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ABSTRACT: Interactions between hydrated Ce\textsuperscript{3+} and various carboxylates are of fundamental interest. Anomalously strong interactions with Ce\textsuperscript{3+} occur when diglycolic acid (DGA) is added into a Ce\textsuperscript{3+} aqueous solution, unlike various other carboxylic acids. Herein, the complex-formation constants of Ce\textsuperscript{3+} with these acids are evaluated via absorption and emission spectra. Hydrated Ce\textsuperscript{3+} emits fluorescence with unity quantum yield; however, addition of various carboxylates statically quenches the fluorescence when Ce\textsuperscript{3+}-carboxylate complexes form because the fluorescence lifetime is constant irrespective of the carboxylate concentration. In the observed static quenching, the complex-formation constants obtained from the absorption and emission spectra \((K_{\text{abs}} \text{ and } K_{\text{em}})\) agree well. The binding of Ce\textsuperscript{3+} by the conjugate Lewis bases, i.e., carboxylates, is approximately inversely proportional to the pH. Adding DGA into the system also statically quenches the fluorescence, but far more efficiently, even in a much weaker solution. We rigorously deduce \(K_{\text{abs}}\) and \(K_{\text{em}}\) of Ce\textsuperscript{3+} with DGA without any approximation using comparable concentrations. Careful fittings provide equivalent \(K_{\text{em}}\) and \(K_{\text{abs}}\) values, and by varying the pH and ionic strength, we confirm that this equivalence is an inherent property of the Ce\textsuperscript{3+}-DGA system. The Lewis acid–base theory cannot explain why DGA binds to Ce\textsuperscript{3+} \(\sim 1000\) times more strongly than the other carboxylates. This anomalously strong binding may be due to a chelate effect caused by the DGA’s central oxygen atom, which forms a five-membered ring with the conjugate Lewis bases of DGA; double chelate rings can also form, while bis-deprotonated DGA binds to Ce\textsuperscript{3+}, facilitated by the central oxygen. Therefore, DGA enables efficient quenching through the chelate effect when it binds to Ce\textsuperscript{3+}.

INTRODUCTION

Highly coordinated lanthanoid cations have attracted considerable attention for their optical, magnetic, and catalytic properties, and therefore, lanthanoid cations play an important role in many interesting applications such as phosphors and sensors. Owing to their luminescent nature, lanthanoid cations have often been incorporated into inorganic phosphors for luminescent applications. Trivalent lanthanoid cations have also been used for sensor applications, e.g., a sensor for detecting physiological phosphates and phosphate-containing biomolecules. Among rare-earth elements, cerium is the most abundant and is thus an inexpensive, accessible raw material. In addition, its trivalent cation, Ce\textsuperscript{3+}, exhibits some biologically important properties such as antiseptic and virus-removal characteristics and potential anticancer activities, and it promotes the proliferation of fibroblasts and osteoblasts. Because Ce\textsuperscript{3+} is similar to Ca\textsuperscript{2+} in terms of its outermost electron configuration, Ce\textsuperscript{3+} is expected to provide various biological effects, which enables replacing biomolecules in vivo. Therefore, understanding the fundamental properties of Ce\textsuperscript{3+} and its interactions with other molecules is extremely important, especially from the viewpoint of potential applications.

Hydrated Ce\textsuperscript{3+} doped into a host material has been studied, and its absorption and emission bands are well assigned. For Ce\textsuperscript{3+} doped into lanthanum(III) ethylsulfate nonahydrate (Ce:LaES), five absorption bands appear in the region between 37 and 51 \(\times\) \(10^{3}\) cm\(^{-1}\) (196–270 nm) at room temperature, whereas at the liquid-nitrogen temperature, two resolved fluorescence bands appear at 30 and 32 \(\times\) \(10^{3}\) cm\(^{-1}\) (313–333 nm). Nine aqua ligands in \(\text{[Ce(H}_{2}\text{O})_9\text{]}^3+\) are arranged around the center Ce\textsuperscript{3+}, defining the vertices of a triaugmented triangular prism with a tricapped trigonal prismatic molecular geometry. The radius of Ce\textsuperscript{3+} is similar to that of La\textsuperscript{3+}; thus, Ce\textsuperscript{3+} can be doped into LaES without significantly changing its
hydrated Ce³⁺ cations in the aqueous solution are excited in good agreement with the absorption spectra. Even if the hydration time of 0.4 ns and produces the excited-state ion, Ce³⁺ in Ce:LaES decays in 27 ns. A very fast partial dissociation of a water ligand out of [Ce(H₂O)₉]³⁺ is in equilibrium with [Ce-(H₂O)₈]³⁺. Increasing the temperature of the aqueous solution changes the absorption spectrum, except at some isosbestic points, and increases the intensity of the absorption band at 34 × 10³ cm⁻¹. In the Ce:LaES crystal, even if the amount of doped Ce³⁺ is increased or the crystal is thickened, the absorption band near 34 × 10³ cm⁻¹ does not appear. In addition, adding an acid such as HClO₄ does not change the absorption spectrum, which suggests that the additional absorption band cannot be attributed to chemical species that can be created by the proton dissociation of the coordinated water molecules such as [Ce(H₂O)(OH)]²⁺. The ²D Kramers doublet does not split into more than five states. In this way, [Ce(H₂O)₈]³⁺ can coexist with [Ce-(H₂O)₉]³⁺ in the aqueous solution.

According to X-ray scattering studies on the structures of hydrated lanthanoid metal ions in aqueous solutions, the partial dissociation of a water ligand out of [Ce(H₂O)₈]³⁺ is not necessarily anomalous. The lanthanoid ions from La³⁺ to Nd³⁺ have nine-water coordinate structures, and Nd³⁺ to Tb³⁺ have both nine-water and eight-water coordinate structures. When Ce³⁺ is in an aqueous solution, the fluorescence shifts to 28 × 10³ cm⁻¹ (357 nm), which is a lower wavenumber (longer wavelength) than that from Ce³⁺ in Ce:LaES. The fluorescence excitation spectra of the aqueous Ce³⁺ solution are in good agreement with the absorption spectra. Even if the hydrated Ce³⁺ cations in the aqueous solution are excited in the five absorption bands of [Ce(H₂O)₈]³⁺ or in that of [Ce(H₂O)]²⁺, i.e., 34 × 10³ cm⁻¹, the fluorescence maximum remains unchanged at 28 × 10³ cm⁻¹ with unity quantum yield.

The fluorescence lifetime of Ce³⁺ in an aqueous solution is 45 ns, whereas Ce³⁺ in Ce:LaES decays in 27 ns. A very fast aqua ligand dissociation of [Ce(H₂O)₈]³⁺ in the excited state was previously investigated; one water molecule dissociates from [Ce(H₂O)₈]³⁺ in an aqueous solution within the short time of 0.4 ns and produces the excited-state ion, *[Ce-(H₂O)₈]³⁺. Because the water molecules rearrange in the coordination sphere faster than they dissociate, the eight-water coordinate structure would be favorable in the excited state.

Along with the structure and fluorescence of Ce³⁺ in an aqueous solution, interactions (and hence complexes) between Ce³⁺ and the anions of organic compounds such as carboxylates, which are the conjugate Lewis bases, have become increasingly important. This importance is rooted in the potential applications of trivalent lanthanoid ions in diverse areas such as optoelectronics and pharmaceutical sciences. Probing the change in fluorescence from Ce³⁺ enables understanding the interactions between Ce³⁺ and other chemical species such as carboxylates because the luminescence is highly sensitive to the environment. Generally, the fluorescence of Ce³⁺ is known to be normally quenched upon complexation with carboxylates. This suppression of the fluorescence is explained by an electron transfer from the excited 5d electron of Ce³⁺ to a closely lying π* orbital of a ligand. An electron can also be completely transferred from the excited Ce³⁺ to persulfate anions via photooxidation. However, some carboxylates do not suppress the fluorescence of Ce³⁺, for example, tris(pyrazine-2-carboxylato)cerium(III) is known to be emissive. The metal-to-ligand charge transfer occurs predominantly from Ce³⁺ to the ligand’s pyrazine moiety, which is strongly electron accepting. The interactions between trivalent metal ions including Ce³⁺ and polymethacrylates in aqueous solutions have also been investigated.

In this study, we discover anomalously strong interactions between hydrated cerium(III) cations (Ce³⁺) and diglycolic acid (DGA), also known as 2-(carboxymethyloxy)acetic acid, while studying the complex formation of hydrated Ce³⁺ with a series of carboxylic acids in aqueous media. Remarkably, a DGA solution more efficiently quenches the fluorescence from Ce³⁺ than the other carboxylic acid solutions, even though it is two to three orders of magnitude less concentrated. These interactions can be observed by adding different carboxylic acids to the solutions and then observing the changes in the absorption and fluorescence of hydrated Ce³⁺. We carefully determine the constants of complex formation from the absorption and emission spectra, Kabs and Kem, when hydrated Ce³⁺ ions interact with the various types of carboxylic acids. The focus is on how the constants of complex formation between Ce³⁺ and DGA can be rigorously determined, and whether the individual complex-formation constants, Kabs and Kem, obtained from the absorption and emission spectra are the same or different. We also analyze the obtained Kabs and Kem in the aqueous Ce³⁺–DGA system to separate the apparent complex-formation constants, Kabs and Kem, which depend on the type of carboxylate, enables interpreting the interactions between Ce³⁺ and various carboxylates. Understanding the fundamental behavior of Ce³⁺ in aqueous media with carboxylic acids remains extremely important from the viewpoint of applications that use Ce³⁺.

RESULTS AND DISCUSSION

As the concentration of carboxylic acid increases, the absorption spectra of Ce³⁺ in aqueous solutions gradually change shape, except at some isosbestic points. Some new peaks appear with the increasing DGA concentration, while others decrease in intensity. The spectrum of a pure Ce³⁺ solution has an absorption maximum (λmax) of 726 M⁻¹ cm⁻¹ at 40 × 10³ cm⁻¹ (250 nm). Figure 1a shows how the absorption spectra of Ce³⁺ change as a function of the concentration of DGA. Figure 1b shows the difference spectra between the Ce³⁺–DGA solutions and their Ce³⁺ counterpart, thus representing only the changes in the spectra.

The isosbestic points indicate that the solution system includes two Ce³⁺-related species that are equilibrated at a constant pH. Therefore, the apparent complex-formation constant can be given by

\[ K_{abs} = \frac{\sum [CeL]}{[Ce^{3+}] \sum [L]} \]

(1)
where \( \sum [CeL] \) and \( \sum [L] \) represent the total concentrations of all one-to-one complexes and all ligand species, respectively. With the total concentrations of Ce\(^{3+}\) and ligands L, namely, \([Ce^{3+}]_0 = [Ce^{3+}] + \sum [CeL]\) and \([L]_0 = \sum [L] + \sum [CeL]\), the absorbance \( A \) is given by

\[
A = e_{Ce}[Ce^{3+}]_0 + e_{CeL} - e_{Ce}[P - \sqrt{Q}]
\]  

(2)

with \( P = [Ce^{3+}]_0 + [L]_0 + K_{bs}^{-1} \) and \( Q = P^2 - 4[Ce^{3+}]_0[L]_0 \), where \( e_{Ce} \) and \( e_{CeL} \) are the apparent absorption coefficients of Ce\(^{3+}\) and its complex species, respectively. Therefore, the complex-formation constants \( K_{bs} \) of Ce\(^{3+}\) with DGA can be analytically deduced from the absorption spectra using the nonlinear least-squares method with eq 2 without any approximation. Equation 2 is explicitly derived in the Supporting Information (SI).

Meanwhile, the changes in the fluorescence emission, however, also enable deducing the complex-formation constants, \( K_{em} \). Ce\(^{3+}\) emits fluorescence with a quantum yield of unity, and the fluorescence lifetime is 45 ns. Figure 2 shows changes in the fluorescence of Ce\(^{3+}\) and the excitation spectrum when DGA is added at different concentrations. Regardless of the concentration, the shape of the excitation spectra is in good agreement with that of the absorption spectra. According to this excitation spectrum, only Ce\(^{3+}\) emits fluorescence, and its lifetime is still 45 ns. Thus, the fluorescence of Ce\(^{3+}\) is statically quenched by DGA.

When fluorescence is statically quenched by the added ligand species, the complex-formation constant \( K_{em} \) can also be deduced from changes in the emission spectra. Thus, \( K_{em} \) of Ce\(^{3+}\) is defined in the same way as \( K_{bs} \) in eq 1 as

\[
K_{em} = \frac{\sum [CeL]}{[Ce^{3+}] \sum [L]}
\]  

(3)

With \([Ce^{3+}] = [Ce^{3+}]_0/(1 + K_{em} \sum [L])\), \( \sum [CeL] = [Ce^{3+}]_0 K_{em} \sum [L]/(1 + K_{em} \sum [L])\), and \([L]_0 = \sum [L] + \sum [CeL]\), the quadratic equation in terms of \( \sum [L] \) can be derived, which is given by

\[
\sum [L] = -R + \sqrt{S}/2K_{em}
\]  

(4)

with \( R = K_{em}[Ce^{3+}]_0 - K_{em}[L]_0 + 1, \) and \( S = R^2 + 4K_{em}[L]_0 \).

Therefore, the relative quantum yield with and without ligand quenchers can be given by

\[
\frac{\phi}{\phi_0} = \frac{[Ce^{3+}]_0}{[Ce^{3+}]_0} = \frac{1}{1 + K_{em} \sum [L]} = \frac{2}{-R + 2 + \sqrt{S}}
\]  

(5)

Equation 5 is explicitly derived in the SI.

In the Ce\(^{3+}\)–DGA system, Stern–Volmer plots for \( \phi_0/\phi - 1 \) are not proportional to \([DGA]_0 \) because \([DGA]_0 \) is comparable to \([Ce^{3+}]_0 \). With eq 5, however, the complex-formation constants, \( K_{em} \) of Ce\(^{3+}\) with DGA can be analytically deduced from the changes in the emission spectra using the nonlinear least-squares method without any approximation.

With eqs 2 and 5, we deduce the values of \( K_{bs} \) and \( K_{em} \), respectively, obtained at some of the adjusted pH points by performing nonlinear curve fittings. Table 1 compares the values of \( K_{bs} \) and \( K_{em} \) at various pH in the Ce\(^{3+}\)–DGA system.

Note that the form of hydrated Ce\(^{3+}\) is not a Volmer plot for \( \lambda \). Figure 3 shows how the absorbance of Ce\(^{3+}\) changes when DGA is added at different concentrations to solutions.
shown in Table 1. Assuming the estimated parameters, the accuracy of the best estimated value of quantum yield ($\phi$) as a function of the concentration of DGA, $K_\text{abs}$ and $K_\text{em}$ can be deduced, which is more straightforward because there is only one unknown parameter. Figure 4 shows the change in the absorbance of Ce$^{3+}$ as a function of the DGA concentration and analytical fits for each pH. For comparison purposes, these plots are merged in Figure S1 of the SI.

![Figure 3](https://example.com/figure3.png)

**Figure 3.** Changes in the absorbance of Ce$^{3+}$ as a function of the DGA concentration and analytical fits for each pH. For comparison purposes, these plots are merged in Figure S1 of the SI.

Table 1. Complex-Formation Constants, $K_\text{abs}$ and $K_\text{em}$ between Ce$^{3+}$ and DGA at Various pH in Aqueous Solutions$^a$ Obtained Using Absorption and Emission Spectra, Respectively,$^b$ with the Relative Uncertainty of $K_\text{abs}$ with Respect to $K_\text{em}$

| pH | $K_\text{abs}$/10$^3$ M$^{-1}$ | $K_\text{em}$/10$^3$ M$^{-1}$ | $\frac{K_\text{em} - K_\text{abs}}{K_\text{abs}} \times 100$/% |
|----|----------------|----------------|----------------------------------|
| 2.00 | 2.06 | 2.05 | 0.49 |
| 2.50 | 10.3 | 11.8 | 14.6 |
| 3.00 | 53.7 | 46.6 | 13.2 |
| 3.70 | 114 | 112 | 1.75 |
| 4.70 | 199 | 192 | 3.52 |

$^a$ Ionic strength $I = 0.1$ M at room temperature ($\sim$20 °C). $^b$ Acid dissociation constants of DGA: $p$K$^a_{\text{DGA}} = 2.79$, $p$K$^b_{\text{DGA}} = 3.93$ at 20 °C.$^5$

![Figure 4](https://example.com/figure4.png)

**Figure 4.** Changes in the quantum yield ($\phi$) of Ce$^{3+}$ as a function of the DGA concentration and analytical fits for each pH. For comparison purposes, these plots are merged in Figure S2 of the SI.

from $\sim$0.5 to $\sim$15%. Presumably, this variation arises because another unknown parameter must be handled in addition to $K_\text{abs}$. Even under these conditions, $K_\text{abs}$ and $K_\text{em}$ can be expected to agree within the attained accuracy from the fact that the fluorescence of Ce$^{3+}$ is statically quenched by DGA. Accordingly, the fluorescence lifetime is constant, irrespective of the amount of DGA.

The same experiments were carried out with other carboxylic acids to validate how $K_\text{abs}$ and $K_\text{em}$ are obtained. The changes in the absorption spectra with some isosbestic points are the same as those in the case of DGA. However, changes in the absorption spectra only appear when the concentration of each carboxylic acid is much higher than that of Ce$^{3+}$. When $[\text{L}]_0 \gg [\text{Ce}^{3+}]_0$, the Benesi–Hildebrand approximation can be used as $\sum([\text{CeL}]) \approx [\text{Ce}^{3+}]_0[\text{L}]_0/([\text{Ce}^{3+}]_0 + [\text{L}]_0 + K_\text{abs}^{-1})$, which is valid if $\sum([\text{CeL}]) \ll [\text{Ce}^{3+}]_0[\text{L}]_0$. We can then deduce

$$\frac{[\text{L}]_0}{A - A_0} = \frac{1}{K_\text{abs}(A_0 - A_0)} + \frac{[\text{Ce}^{3+}]_0 + [\text{L}]_0}{A_0 - A_0} \quad (6)$$

where $A_0 = \varepsilon_{\text{Ce}[\text{Ce}^{3+}]_0}$ and $A_\infty = \varepsilon_{\text{Ce}[\text{L}]_0}$. In the case of the other carboxylic acids besides DGA, the plots of $[\text{Ce}^{3+}]_0/(A - A_0)$ vs $([\text{Ce}^{3+}]_0 + [\text{L}]_0)$ yield straight lines, as shown in Figure S5, which validates eq 6. In addition, $K_\text{abs}$ obtained from eq 6 using the approximation coincides with that obtained from the original equation, i.e., eq 2, in a series of carboxylic acids. Thus, the $K_\text{abs}$ values of Ce$^{3+}$ with other carboxylic acids are determined by the linear least-squares fit using eq 6, shown in Figure 5.

The fluorescence of Ce$^{3+}$ is also statically quenched when carboxylic acids are added, similar to the case with DGA because the fluorescence lifetime is independent of the concentration of carboxylic acids. Figure 6 shows Stern–Volmer plots for quenching with carboxylic acids. Unlike the cases with DGA, owing to the excess concentration of
carboxylic acid relative to that of Ce³⁺, the proportional relation, i.e., \( (\phi_0 / \phi - 1) vs [L]_0 \) holds. Therefore, \( K_{em} \) can be derived from the slope of the Stern–Volmer plots.

Table 2 compares \( K_{abs} \) and \( K_{em} \) of the various carboxylic acids other than DGA. For the measurements, each pH value was set to be approximately the acid dissociation constant, \( pK_a \), except for glutaric acid (GLA), also known as pentanedioic acid. Note again that the form of hydrated Ce³⁺ is not affected by hydrolysis or condensation in this pH range.\(^{36,37}\) As expected for static quenching, as in the case of DGA, the values of \( K_{abs} \) agree well with those of \( K_{em} \) within the accuracy from \( \pm 0.7 \) to \( \pm 9\% \). This agreement clearly indicates that Ce³⁺ forms a complex with carboxylates, and these complexes are not emissive, which is the typical static quenching. Therefore, \( K_{abs} \) should be equivalent to \( K_{em} \). The range of the relative uncertainties, \( (K_{abs} - K_{em}) / K_{abs} \times 100 \), in Table 2 is smaller than that in Table 1, which indicates better agreement between \( K_{abs} \) and \( K_{em} \) in these systems than that in the Ce³⁺–DGA system. For deducing \( K_{abs} \) for the Ce³⁺–carboxylate systems other than DGA, eq 6 is more straightforward than eq 2 because it does not require two unknown parameter fittings.

These results are consistent with the previously obtained cases in which \( K_{abs} \) and \( K_{em} \) are equivalent in the Ce³⁺–DGA system. Notably, however, the values of \( K_{abs} \) and \( K_{em} \) in the Ce³⁺–

Figure 5. Plots of \( [\text{Ce}^{³⁺}]_0 / (A - A_0) vs [\text{Ce}^{³⁺}]_0 + [L]_0 \) for various carboxylic acids other than DGA. Solid lines are analytical fits. For comparison purposes, these plots are merged in Figure S3 of the SI.

Figure 6. Stern–Volmer plots, \( (\phi_0 / \phi - 1) vs [L]_0 \) for various carboxylic acids excluding DGA. [L]₀ is the total concentration of each carboxylic acid. Solid lines are analytical fits. For comparison purposes, these plots are merged in Figure S4 of the SI.
Table 2. Complex-Formation Constants, $K_{\text{abs}}$ and $K_{\text{em}}$, between Ce$^{3+}$ and Carboxylic Acids Other Than DGA in Aqueous Solutions Obtained from Their Absorption and Emission Spectra, Respectively, with the Relative Uncertainty of $K_{\text{abs}}$ with Respect to $K_{\text{em}}^{a}\text{b}$

| ligand          | pH    | $K_{\text{abs}}$/M$^{-1}$ | $K_{\text{em}}$/M$^{-1}$ | $(\log K_{\text{abs}} - \log K_{\text{em}}) \times 100/\%$ |
|-----------------|-------|--------------------------|--------------------------|---------------------------------------------------|
| CH$_3$COOH      | 4.73  | 42.0                     | 40.7                     | 3.10                                              |
| CH$_3$CH$_2$COOH| 4.87  | 44.6                     | 44.9                     | 0.67                                              |
| CICH$_2$COOH    | 2.87  | 8.32                     | 8.63                     | 3.73                                              |
| CF$_3$COOH      | 0.60  | ~0                       | ~0                       |                                                   |
| CH$_3$OCH$_2$COOH| 3.53  | 36.8                     | 40.2                     | 9.24                                              |
| CH$_2$(CH$_2$COOH)$_2$ : GLA| 3.50  | 21.9                     | 23.4                     | 6.85                                              |
|                 | 4.00  | 48.2                     | 46.1                     | 4.36                                              |
|                 | 4.50  | 116                      | 119                      | 2.59                                              |

$^{a}$Ionic strength $I = 0.1$ M at room temperature (~20 °C). $^{b}$Note that each solution involving a monocarboxylic acid was set to a particular pH to attain equal rates of protonation and deprotonation, such that each value of the adjusted pH became equivalent to that of pK$_a$ at 20 °C in parentheses. $^{44}$ Acid dissociation constants of GLA: pK$^{\text{GLA}}_{2a} = 4.34$, pK$^{\text{GLA}}_{2b} = 5.41$ at 20 °C. $^{45}$ DGA system are anomalously large; indeed, they are two to three orders of magnitude larger than those in the series of carboxylic acids, which prompted us to further investigate the interactions between Ce$^{3+}$ and DGA.

When Ce$^{3+}$ forms a complex with carboxylate, the carboxylate donates a lone pair of electrons to the ion, which is true for all carboxylates in our experiments. According to Lewis’s definition of acids and bases, the carboxylate serves as a base, whereas Ce$^{3+}$ behaves as an acid, and hence, they form a Werner-type complex. In addition, Ce$^{3+}$ and carboxylates are categorized into hard acids and bases, respectively, and therefore, Ce$^{3+}$ can form complexes with carboxylates, which are the conjugates of Lewis bases, through bonding that is mostly governed by Coulombic interactions. Similarly, however, the protonation of the carboxylates can also be regarded as a hard acid–hard base complexation reaction.

The mechanism underlying the association and dissociation of Werner-type complexes is compatible with the association and dissociation of carboxylates and protons. This suggests that stronger carboxylic acids, which have a stronger tendency to release protons, are also preferable for avoiding the formation of complexes with Ce$^{3+}$.

Figure 7 exhibits the relationship between pK$_a$ and $K_{\text{abs}}$ (or $K_{\text{em}}$) in the series of monocarboxylic acids in Table 2. The relation between pK$_a$ and $K_{\text{abs}}$, including $K_{\text{em}}$ can be seen to yield a straight line; weaker acids, which indicate a larger pK$_a$ and associate more strongly with protons, also easily bind to Ce$^{3+}$. The slope of the line is close to one, which indicates a typical relationship between hard acids and hard bases. However, note that the slope of the line cannot be determined accurately because trifluoroacetate is unlikely to form a complex with Ce$^{3+}$; i.e., the antilogarithm is not allowed to be exactly zero. Here, we approximate $K_{\text{abs}}$ (or $K_{\text{em}}$) of Ce$^{3+}$ with trifluoroacetate to a number that can be regarded as zero within experimental accuracy while recognizing ambiguity. The slope of the relation between pK$_a$ and $K_{\text{abs}}$ (or $K_{\text{em}}$) directly depends on how the carboxylates interact with Ce$^{3+}$ in comparison with H$^+$; the influential factors are the size of Ce$^{3+}$, the distance between Ce$^{3+}$ and the carboxylates, and the charge-shielding effect caused by the inner electrons of Ce$^{3+}$.

The Aqua ligands surrounding Ce$^{3+}$ can also cause the shielding effect if the carboxylates can react with Ce$^{3+}$ in its outer-sphere region. Nevertheless, our results with monocarboxylic acids clearly suggest that a Lewis base that easily binds to a Lewis acid H$^+$ also easily binds to a central ion Ce$^{3+}$, which is another Lewis acid. We conclude that this finding is consistent with the conventional theory on the relationship between the basicity of ligands and complex formation.$^{42-45}$

Now let us consider dicarboxylic acids, i.e., GLA in Table 2 and DGA in Table 1, which cannot be compared by extrapolating the line in Figure 7. Figure 8 shows how the complex-formation constants, $K_{\text{abs}}$ and $K_{\text{em}}$, increase as a function of pH. The solid line for GLA is the least-squares visual guide for pH ≤ 3.0. The vertical dotted lines are visual guides for the pK$_a$ values of DGA and GLA.

![Figure 7](image-url)  
Figure 7. Relationship between pK$_a$ and $K_{\text{abs}}$ (or $K_{\text{em}}$) of Ce$^{3+}$ with the series of aqueous monocarboxylic acid solutions.

![Figure 8](image-url)  
Figure 8. $K_{\text{abs}}$ and $K_{\text{em}}$ of Ce$^{3+}$ with two different dicarboxylic acids (DGA and GLA, as indicated by superscripts) as a function of pH. The solid line for GLA is the least-squares fit, whereas the solid line for DGA is a visual guide for pH ≤ 3.0. The vertical dotted lines are visual guides for the pK$_a$ values of DGA and GLA.
function of pH. Specifically, for the case of GLA, both $K_{abs}^{GLA}$ and $K_{em}^{GLA}$ (which are equivalent) increase proportionally to the pH. At pH = pK$_{a2}^{GLA}$, however, $K_{abs}^{GLA}$ (or $K_{em}^{GLA}$) can be compared with $K_{abs}$ (or $K_{em}$) of monoca rboxylates, which allows us to observe that $K_{abs}^{GLA}$ (or $K_{em}^{GLA}$) is near the trend line in Figure 7. This finding suggests that in the case of GLA, other interactions beyond the strength of Lewis bases seem not to significantly influence the formation of complexes with Ce$^{3+}$.

Beyond the case of GLA, however, we can clearly recognize how the complex-formation constants of DGA, $K_{abs}^{DGA}$ and $K_{em}^{DGA}$, are anomalously larger than those of the dicarboxylic acid GLA. Surprisingly, $K_{abs}^{DGA}$ and $K_{em}^{DGA}$ are three orders of magnitude larger than $K_{abs}$ and $K_{em}$, respectively.

Besides the Lewis base property, the molecular structures of the dicarboxylic acids might also influence the complex formation, as multidentate ligands potentially lead to interactions, owing to a chelate effect.$^{45-47}$ Both GLA and DGA can be dissociated successively with two protons, thereby changing their forms, i.e., the deprotonated GL$^{-}$ and DG$^{-}$ and bis-deprotonated GL$^{2-}$, DG$^{2-}$ species. The dianionic species GL$^{2+}$ and DG$^{2-}$ are well known as bidentate and tridentate ligands,$^{47,48}$ which can then form ring structures with Ce$^{3+}$, i.e., chelate-ring structures. The ether oxygen of DG$^{2-}$ was already discovered to have a strong stabilizing effect in chelate rings.$^{47,48}$ In fact, DG$^{2-}$ forms complexes with various metallic cations such as Eu$^{3+}$,$^{49}$ Co(II),$^{50}$ Cu(II),$^{51}$ Ca(II), and Ba(II),$^{52}$ with the ether oxygen stabilizing the chelate structure. This property of DGA has been exploited to remove rare-metal ions from an aqueous solution via the interactions of polymer-functionalized DGA with Ce$^{3+}$ and Nd$^{3+}$. The findings of those studies support the anomalous $K_{abs}^{DGA}$ and $K_{em}^{DGA}$ in our series of measurements and analyses.

The chelate effect is known to stabilize complexes, owing to increased entropy. GL$^{2-}$ can indeed form an eight-membered ring while forming complexes with Ce$^{3+}$; however, the chelate effect of GL$^{2-}$ does not seem significant, presumably because of the eight-membered ring, which provides such a large multimembered ring that the distortion is large. By contrast, in addition to its two carboxyl groups, DGA has an oxygen atom that can donate a lone pair of electrons to the center ion, which suggests DG$^{2-}$ can work as a tridentate ligand while interacting with Ce$^{3+}$. Therefore, DG$^{2-}$ and Ce$^{3+}$ can form two five-membered rings, which results in a double chelate effect. The chelate effect can be amplified when a five-membered ring is formed and when the number of rings increases. Furthermore, the tripod-bonding structures formed by Ce$^{3+}$ and DG$^{2-}$ would have shape flexibility in three dimensions because Ce$^{3+}$ is highly coordinated by nine ligands. The double chelate effect with five-membered rings could plausibly explain why $K_{abs}^{DGA}$ and $K_{em}^{DGA}$ are so much larger than those of other ligands. In Figure 8, the magnitudes of $K_{abs}^{DGA}$ and $K_{em}^{DGA}$ vastly differ from those of $K_{abs}^{GLA}$ and $K_{em}^{GLA}$; this difference may be caused by the oxygen atom in the DGA molecule, which produces the chelate effect. When the pH surpasses pK$_{a2}^{DGA}$, the values of $K_{abs}^{DGA}$ and $K_{em}^{DGA}$ begin to level off, indicating that DG$^{2-}$ becomes the major component and is saturated.

Figure 9 shows how the ionic strength affects $K_{abs}^{DGA}$ and $K_{em}^{DGA}$, which are determined at several pH values. Because $K_{abs}^{DGA}$ and $K_{em}^{DGA}$ are equivalent, only $K_{abs}^{DGA}$ is represented in the figure. Clearly, $K_{em}^{DGA}$ decreases with the increasing ionic strength only in the region of the low ionic strength, especially $K_{em}^{DGA}$ at high pH. This initial decreasing trend is due to the decreased activities of the ion species, which do not change much in the region of high ionic strength. The activity coefficient is largely determined by the charge of the ion, and therefore, at higher pH, the increasing ionic strength considerably affects the activity because DG$^{2-}$ becomes more important and plays a crucial role in forming complexes.

In principle, the apparent complex-formation constants, $K_{abs}^{DGA}$ and $K_{em}^{DGA}$, of the Ce$^{3+}$–DGA system can be separated into those of individual reaction steps. In fact, the pH dependence of $K_{abs}^{DGA}$ and $K_{em}^{DGA}$ is an obvious consequence of the protolytic equilibria of DGA and its complex species with Ce$^{3+}$: Figure 10 shows a plausible mechanism of complex formation between Ce$^{3+}$ and DGA.
Throughout the series of experiments on the Ce$^{3+}$–DGA system with various pH and ionic strength conditions, the values of $K_{\text{abs}}$ and $K_{\text{em}}$ in this system are indeed equivalent, although they are much larger than those in the other carboxylic acid systems. Unfortunately, however, decomposing $K_{\text{abs}}$ or $K_{\text{em}}$ into $K_{\text{ML}}$, $K_{\text{MLH}}$, and $K_{\text{MLH2}}$ for each ionic strength with eq 7 can only be successful while constraining three parameters at a time with only five data points for each ionic strength would be very difficult. Nevertheless, Figure 9 allows us to assume that $K_{\text{MLH2}} \approx 10^{-10} \text{ M}^{-1}$ would be reasonable orders of magnitude because the major species at pH 2.00 would be DGA$^2$. Additionally, we noticed that the optimized $K_{\text{ML}}$ and $K_{\text{MLH}}$ values hardly vary within the assumed range of $K_{\text{MLH2}}$. For the ionic strength $I = 0.1$, values of $K_{\text{ML}} \approx 2.18$–2.19 $\times 10^5 \text{ M}^{-1}$ and $K_{\text{MLH}} \approx 5.23$–5.30 $\times 10^4 \text{ M}^{-1}$ are attained. Table 3 summarizes the decomposed values of $K_{\text{ML}}$ and $K_{\text{MLH}}$ from $K_{\text{DGA}}$ for each ionic strength. In the cases of $I = 0.01$ and 0.05, a further constraint is required to improve $K_{\text{ML}}$ and $K_{\text{MLH}}$, which are optimized within the possible range of $K_{\text{MLH}}$ in addition to the constraint on $K_{\text{MLH2}}$. Interestingly, however, $K_{\text{ML}}$ hardly varies within the wide range of $K_{\text{MLH}}$ and $K_{\text{MLH2}}$. Therefore, the results for $K_{\text{ML}}$ are roughly more reliable than the others. Indeed, we can reliably recognize that dicarboxylate DGA$^2$ exhibits an anomalously larger $K_{\text{ML}}$ than the other carboxylates.

Further, we can directly compare the value of $K_{\text{ML}}$ for the Ce$^{3+}$–DGA$^2$ complex with those of all its Ce$^{3+}$–carboxylate counterparts. Using the same stepwise-formation scheme, we can deduce $K_{\text{ML}}$ for all of the other carboxylates while assuming that only the deprotonated carboxylates are capable of binding to Ce$^{3+}$. For the monocarboxylates, each $K_{\text{ML}}$ can be simply calculated using $K_{\text{abs}}$ or $K_{\text{em}}$ with the pH and $pK_a$ whereas nonlinear fits using three pH values enable deducing $K_{\text{ML}}$ and $K_{\text{MLH}}$ for GL$^2$. Table 4 summarizes the values of $K_{\text{ML}}$ and $K_{\text{MLH}}$ for all of the other carboxylates besides DGA$^2$. The value of $K_{\text{ML}}$ for acetate is in good agreement with that in the previous work, indicating the reliability of our way to obtain $K_{\text{ML}}$. Therefore, determining $K_{\text{ML}}$ for Ce$^{3+}$ bound by the series of carboxylates is meaningful. The anomaly of DGA$^2$ and DGA$^-$ becomes more pronounced when comparing $K_{\text{ML}}$ values between DGA$^2$ and the other carboxylates. Presumably, as discussed above, the oxygen atom in the DGA$^2$ carboxylate can stabilize the Ce$^{3+}$–DGA$^2$ complexes by creating two five-membered rings, thus demonstrating the chelate effect.

Table 3. Decomposed Complex-Formation Constants, $K_{\text{ML}}$, and $K_{\text{MLH}}$ of Ce$^{3+}$ with DGA$^2$ and DGA$^-$, Respectively

| Ionic strength $I$/M | $K_{\text{ML}}$/$10^3$ M$^{-1}$ | $K_{\text{MLH}}$/$10^4$ M$^{-1}$ |
|----------------------|-----------------------------|-----------------------------|
| 0.01                 | 50.7–51.3                   | 6.00–20.0$^{b}$             |
| 0.05                 | 2.98–3.20                   | 4.00–9.00$^{b}$             |
| 0.1                  | 2.18–2.19                   | 5.23–5.30                   |
| 0.2                  | 2.03–2.04                   | 3.23–3.30                   |
| 0.7                  | 1.31–1.32                   | 1.75–1.83                   |

$^{a}$Note that $K_{\text{MLH2}} \approx 10^{-10}$ M$^{-1}$ is assumed, as described in the text. $^{b}$Range of $K_{\text{MLH}}$ is also assumed to have high-quality fits.

Table 4. Decomposed Complex-Formation Constants, $K_{\text{ML}}$, and $K_{\text{MLH}}$ of Ce$^{3+}$ with the Carboxylates Other Than DGA$^2$,$^{a}$,$^{b}$

| Carboxylates | $K_{\text{ML}}$/M$^{-1}$ | $K_{\text{MLH}}$/M$^{-1}$ |
|-------------|-------------------------|-------------------------|
| CH$_3$COO$^-$ | 68.2–70.4               | 0                       |
| CH$_2$CH$_2$COO$^-$ | 72.7–73.2         | 0                       |
| CIC$_3$COO$^-$ | 13.7–14.3              | 0                       |
| CF$_3$COO$^-$ | ~0                     | 0                       |
| CH$_2$OCH$_2$COO$^-$ | 77.2–84.3          | 0                       |
| CH$_3$(CH$_2$COO)$^2-$ | 577–673           | 132–139                 |

$^{a}$Ionic strength $I = 0.1$ M at room temperature (~20 °C). $^{b}$Note that $K_{\text{MLH}} = 0$ M$^{-1}$ for monocarboxylates and $K_{\text{MLH2}} = 0$ M$^{-1}$ for GL$^2$ are assumed, as described in the text.

chelate effect plays an important role in forming a complex between these species in an aqueous solution. The complex-formation constants of Ce$^{3+}$ with various carboxylates are determined through the changes in the absorption and emission spectra. Although hydrated Ce$^{3+}$ emits fluorescence with unity quantum yield, when Ce$^{3+}$ forms complexes with carboxylates, it becomes nonemissive, which means that the fluorescence of Ce$^{3+}$ is statically quenched by carboxylates, including DGA. This behavior is supported by the good agreement between the $K_{\text{abs}}$ values obtained from the absorption spectra and those $K_{\text{em}}$ obtained from the emission spectra. In the investigated series of monocarboxylates, the binding strength between Ce$^{3+}$ and the conjugate Lewis bases, i.e., carboxylates, is inversely proportional to the acidity strength. Similarly, the conjugate Lewis bases of DGA, i.e., DG$^-$ and DG$^{2-}$, bind to Ce$^{3+}$ in an aqueous solution; however, the rigorously deduced $K_{\text{abs}}$ and $K_{\text{em}}$ values of Ce$^{3+}$ with DGA are three to five orders of magnitude larger than those obtained with other carboxylates as well as another typical dicarboxylate, namely, glutarate. These constants suggest interactions beyond those explained by the Lewis acid–base theory. We propose that this anomalously strong binding between Ce$^{3+}$ and DGA is caused by a chelate effect because of the central oxygen atom in DGA molecules. Specifically, the two conjugate Lewis bases of DGA, i.e., DG$^-$ and DG$^{2-}$, enable forming a five-membered ring with the help of this central oxygen atom. Moreover, double chelate rings can form, which can be created by DG$^{2-}$ and stabilized by its central oxygen. We have also attempted to decompose the apparent complex-formation constants, $K_{\text{DGA}}$ and $K_{\text{DGA}}^{\text{DG}^2}$, of the Ce$^{3+}$–DGA system into individual complex-formation constants. Unfortunately, however, optimizing three unknown parameters made it difficult to find solutions without constraining one or two parameters. A large amount of data would be required to deduce more reliable individual complex-formation constants through the fittings. Nevertheless, our analysis allows us to conclude that the conjugate Lewis bases, DG$^{2-}$ and DG$^-$, bind to Ce$^{3+}$ three to five orders of magnitude more strongly than the other carboxylates. Further efforts should be devoted to revealing the double chelate structure of the complex between Ce$^{3+}$ and DG$^{2-}$ and its properties in a solution, such as the temperature-dependent equilibria of the chelate formation.

**CONCLUSIONS**

While exploring the interactions between hydrated Ce$^{3+}$ and various types of carboxylates, we discovered anomalously strong interactions between Ce$^{3+}$ and DGA. Presumably, a

**METHODS**

**Materials.** Cerium(III) perchlorate nonahydrate Ce(ClO$_4$)$_3$·9H$_2$O was synthesized from Ce$_2$(SO$_4$)$_3$·8H$_2$O and Ba(ClO$_4$)$_2$·3H$_2$O$^{19}$ (Sigma-Aldrich, reagent grade). Ce$_2$(SO$_4$)$_3$·8H$_2$O (7.12 g, 9.99 $\times 10^{-3}$ mol) was dissolved in

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water (100 mL), and the solution was stirred while being kept cool for 2–3 h. Insoluble Ce₂(SO₄)₃·8H₂O was removed with a pleated filter. Ba(ClO₄)₂·3H₂O (11.7 g, 3.00 × 10⁻² mol) in water (50 mL) was gently added to the filtrate, which produced white precipitates. The solution was sufficiently stirred and allowed to sit still overnight. The precipitates were removed by decantation and filtering, and 1 M H₂SO₄ was gradually added 1 μL at a time to the solution while stirring to precipitate the excess Ba²⁺ dissolved in the solution. The Ce₂(SO₄)₃·9H₂O solution was adequately concentrated and used as a stock solution.

Ce₂(C₂H₅SO₄)₃·9H₂O (CeES) was obtained using the method reported by Ketelaar.⁵⁶ Ce₂–DGA system and the Ce³⁺ systems with other carboxylates were performed at least five and three times, respectively. The average of raw data was taken for each data point and used for further analysis. The accuracy of the two values being compared is evaluated using their relative uncertainty, which is defined as δK/K_best, where K_best is the best estimated value and δK is the uncertainty associated with each measurement.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04724.

Explicit derivation of eqs 2 and 5 and plots merged separately from Figures 3–6 in the main text (PDF)

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**Author Contributions**

This manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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