Published in final edited form as:

Chirality. 2012 December ; 24(12): 1055–1062. doi:10.1002/chir.22097.

Chiroptical Spectra of Tetrakis (+)-3-Heptafluorobutyrylcamphorate Ln(III) Complexes with an Encapsulated Alkali Metal Ion: Solution Structures as Revealed by Chiroptical Spectra

Dai Shirotani¹, Kazuaki Yamanari¹, Reiko Kuroda^{2,3}, Takunori Harada^{2,4}, Jamie L. Lunkley⁵, Gilles Muller⁵, Hisako Sato⁶, and Sumio Kaizaki^{7,8,*}

¹Institute for Higher Education Research and Practice, Osaka University, Toyonaka, Osaka, Japan

²Department of Life Science, Graduate School of Arts and Sciences, The University of Tokyo, Meguro, Tokyo, Japan

³Research Institute for Science and Technology, Tokyo University of Science, Noda, Chiba, Japan

⁴Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba, Japan

⁵Department of Chemistry, San Jose State University, San Jose, CA

⁶Department of Chemistry, Faculty of Science, Ehime University, Matsuyama, Japan

⁷Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka, Japan

⁸Venture Business Laboratory, Osaka University, Suita, Osaka, Japan

Abstract

The preparation of tetrakis((+)-hfbc) lanthanide(III) complexes with an encapsulated alkali metal and ammonium ions $M[Ln((+)-hfbc)_4]$ (hereafter abbreviated as M-Ln : (+)-hfbc, (+)-heptafluorobutyrylcamphorate; M, ammonium or benzyl ammonium ions as well as alkali metal ions) was reported and discussed. The electronic circular dichroism (CD) spectra in the intraligand $\pi-\pi^*$ transition of M-Ln were examined in view of the solvent effect. Here, the concentration, alkali metal, and ammonium ion dependences are compared with the solid CD, $^5D_0 \leftarrow ^7F_0$ (Eu(III)) excitation spectra, circularly polarized luminescence, and vibrational circular dichroism. It has been revealed that the dodecahedral eight coordinate DD-8-M-Ln complexes in crystals are equilibrated between the diastereoselectively formed square antiprism eight coordinate SAPR-8-M-Ln and $[Ln((+)-hfbc)_3]$ in EtOH and CH_3CN solutions or between the SAPR-8-M-Ln and DD- $D_{2d}(mmmm)$ -8-M-Ln complexes in $CHCl_3$ solution. The observed CD couplets are found to reflect the exciton CD couplets which are useful to determine the four-bladed SAPR-(*IIII*) absolute configuration around the lanthanide(III) ion.

Keywords

ultraviolet CD; exciton CD; solvent effect; alkali metal ions dependence; concentration dependence; absolute configuration; diastereoselective formation

INTRODUCTION

There have been a number of chiral lanthanide(III) complexes examined from various viewpoints including chemical sensing, biological applications, and chiral catalysis.^{1–10} In order to reveal lanthanide ion recognition on the basis of specific chiroptical spectra–structure relationships, one fundamental piece of information to know is the configurational chirality around labile Ln(III) ions with a variety of coordination polyhedrons in Ln(III) complexes. Chiral macrocyclic tetramine tetracarboxylate octadentate ligands “dota”,^{4,11–13} helical noncovalent d–f tripodes with terdentate chiral ligands, or d–f heterometal dinuclear complexes,^{14–16} as well as chiral 2-hydroxyisophthalamide-, pyridyl diamine-, and 1-hydroxy-2-pyridinone-based ligands¹⁷ result in diastereoselective formation of structurally robust configurational chiral lanthanide(III) complexes, even in solution. Several tris- β -diketonato lanthanide(III) complexes have been used as chiroptical probes for specific recognition of chiral amino acids, amino alcohols, and diols,¹⁸ since the pioneering work of Nakanishi and Dillon.¹⁹ Therein, on the basis of the circular dichroism (CD) couplet near 300 nm in the intraligand π – π^* transition of the β -diketonate ligand, the chiral absolute configuration of organic compounds functioning as chiral bidentate ligands is determined.^{6,19} The signs of the CD couplets depend on the conformation of the bidentate chelates with the bulky groups in the equatorial positions. That is, *R*-bidentate ligands with the anticlockwise (λ) chelate ring conformation give a positive couplet (a positive and a negative CD from the longer wavelength) and vice versa. Assuming a helical-bladed arrangement of the ligand molecules around the central Ln(III) ion in the tetrakis-chelated [Ln(β -diketonato)₃(*R*-bidentate)] complexes with the positive CD couplet, one may suppose that the absolute configuration may be defined as λ . This is true if one bases this determination from the exciton theory. However, it is difficult merely to assume the exciton CD bands in the β -diketonate intraligand π – π^* transition region, since square antiprism eight coordinate SAPR-8-(*ssss*) or –(*ssll*) configurations are more stable than the SAPR-8-(*llll*) (Scheme 1 where *s* and *l* mean the chelation between sites of the same and different squares in SAPR, respectively) when considering steric hindrances. This is confirmed by the X-ray structures of most tetrakis(β -diketonato) lanthanide(III) complexes and molecular mechanics calculations.²⁰ Additionally, there are some examples of configurationally chiral tetrakis(β -diketonato) Ln(III) complexes such as enantiomeric pairs of DD-*D*₂-(*gggg*)-8-Cs[Y(hfac)₄],^{21,22} –Cs[Eu(hfac)₄],²³ –NH₄[Pr(ttf)₄] (ttf, thionyltrifluoroacetate),²⁴ –(Hpip)[Gd(BA)₄] (Hpip, piperidinium and BA, benzoylacetylacetone),²⁵ and SAPR-*D*₂-(*ssss*)-8-(Et₃NH)[Eu(dbm)₄] (dbm, dibenzoylmethanate)²⁶ (Scheme 1). On the other hand, labile tris- or tetrakis-(chiral β -diketonato) Ln(III) complexes such as (+)-hfbc((+)-3-heptafluorobutyrylcamphorate) or (+)-tfac((+)-3-trifluoroacetylcamphorate) (Scheme 2) have been extensively utilized for chiral discrimination by nuclear magnetic resonance (NMR)⁶ and chiroptical techniques consisting of CD or circularly polarized luminescence (CPL).^{12, 27} However, the solution structures were not well characterized. The tetrakis(+)-heptafluorobutyrylcamphorate (hfbc) complexes, [Ln((+)-hfbc)₄][–], are expected to take a stereospecific chiral configuration owing to bulky steric requirements for camphorate groups, as suggested for [Eu((+)-hfbc or (+)-tfac)₃(solvent)][–],²⁸ [Eu((+)-tfac)₄][–],²⁹ or [Eu((+)-tfac)₃(chiral BINAPO) or (TPPO)₂] with phosphine oxide ligands.³⁰

We have embarked to study the chiroptical properties and solution structures of chiral tetrakis(+)-3-heptafluorobutyrylcamphorate Ln(III) complexes with an encapsulated alkali

metal ion, $M^I[Ln((+)\text{-hfbc})_4]$ (hereafter abbreviated as $M\text{-Ln}$). The preliminary reports on the CD, CPL, and vibrational circular dichroism (VCD) studies including the synthesis and the X-ray structure have been published.^{31–34} Recently, the full paper on the CPL study has been reported.³⁵

In this article, the synthesis of novel ammonium–Ln complexes as well as a series of alkali metal ion–Ln complexes will be reported. Of special importance is the solution structure of the $M\text{-Ln}$ complexes, including the chemical species discussed in terms of the solvent effects. The alkali metal or ammonium ions and concentration dependences on the CD in the ultraviolet region with support of the $^5D_0 \leftarrow ^7F_0(\text{Eu(III)})$ excitation spectra, CPL, and VCD will also be discussed.

EXPERIMENTAL

All chemicals were reagent grade and used as received. (+)-Hhfbc was purchased from Sigma-Aldrich without further purification.

Synthesis of the $M^I[Ln((+)\text{-hfbc})_4]$ Complexes

A series of the complexes $M^I[Ln^{III}((+)\text{-hfbc})_4]$ were prepared as follows. $LnCl_3 \cdot nH_2O$ or $Ln(OAc)_3 \cdot nH_2O$ (0.28 mmol) was dissolved in H_2O (15 ml). (+)-Hhfbc (0.84 mmol) was deprotonated by Et_3N in 30 ml of $CHCl_3$. The two solutions were mixed in a separating funnel by shaking. The $CHCl_3$ layer was separated. An excess amount of alkali metal chloride was dissolved in 30 ml of H_2O . This was mixed in a separating funnel again. After the $CHCl_3$ layer was separated, the solution was concentrated to dryness. To the powder, 30 ml of CH_3CN was added. After it was filtered, the filtrate was allowed to stand for several days. Fine needle crystals or powders were obtained.

The preparation of $NH_4[Eu((+)\text{-hfbc})_4]$ was performed with a similar method as $NH_4[Eu(TTA)_4]$ (TTA, 2-thenoylfluoroacetylacetone).²⁴ (+)-Hhfbc (0.84 mmol) was dissolved in 8 ml of EtOH and was deprotonated by NH_3 aq (28%). $Eu(OAc)_3 \cdot 4H_2O$ (0.28 mmol) dissolved in EtOH (2 ml) and H_2O (1 ml) was added. The yellow solution was evaporated to dryness and washed with water. This powder was dissolved in EtOH (15 ml) again, and after a few days, a yellow pure solid was obtained.

The benzylammonium complex was obtained as follows. $PrCl_3 \cdot 7H_2O$ or $Eu(OAc)_3 \cdot 4H_2O$ (0.28 mmol) was dissolved in H_2O (15 ml). (+)-Hhfbc (1.12 mmol) was deprotonated by Et_3N in 30 ml of $CHCl_3$. After these solutions were mixed in a separating funnel, the $CHCl_3$ layer was separated. The $CHCl_3$ layer solution was mixed with 30-ml aqueous solution containing an excess amount of benzylammonium chloride. The mixture was shaken in a separating funnel for a second time. After the $CHCl_3$ layer was separated, the solution was concentrated to dryness. To this powder, 30 ml of CH_3CN was added. After it was filtered, the solution was allowed to stand for several days. Several plate crystals were obtained.

Elemental analyses of all the prepared $M^I[Ln((+)\text{-hfbc})_4]$ complexes are listed in Table S1.

Measurements

Absorption spectra were measured on a Perkin Elmer Lambda-19 spectrophotometer. Solution CD data were collected on a JASCO J-720 W spectropolarimeter at room temperature. The CD measurements were run on solutions of 2–0.01 mM. Solid-state diffuse reflectance CD was obtained on the purpose-built JASCO J-800-KCM spectrometer at the University of Tokyo.

$^5D_0 \leftarrow ^7F_0$ excitation measurements for the Cs–Eu(III) complex were accomplished by using a Coherent-599 tunable dye laser (0.03 nm resolution) with a Coherent Innova Sabre TMS 15 or Innova-70 argon ion laser as a pump source at San Jose State University. The laser dye used in all measurements was rhodamine 6G dissolved in ethylene glycol. Calibration of the emission monochromator (and subsequently the dye laser wavelength) was accomplished by passing scattered light from a low-power He–Ne laser through the detection system. The error in the dye laser wavelength is assumed to equal the resolution of the emission monochromator (0.1 nm). The optical detection system consisted of a focusing lens, long pass filter, and 0.22-m monochromator. The emitted light was detected by a cooled EMI-9558B photomultiplier tube operating in photon-counting mode. All measurements were performed in quartz cuvettes with a path length of 0.4 or 1.0 cm.

RESULTS AND DISCUSSION

Preparation and Characterization

The M–Ln complexes were synthesized by the modified method for $[Ln(hfac)_3]^{36}$ with the use of $CHCl_3$ and Et_3N instead of ether and aqueous ammonia. It is interesting to note that the reaction conditions for preparation of $Na[Ln((+)-hfbc)_4] \cdot CH_3CN$ are based on a Ln(III) : (+)-hfbc[−] mole ratio of 1:3 but not stoichiometric ratio of 1:4 in the reaction mixture. The source of Na⁺ ion is originated from desiccant anhydrous Na_2SO_4 , which is insoluble in chloroform. The Na–Ln complexes were only prepared for Ln(III) ions with smaller atomic numbers than Gd(III). The other M–Ln complexes (M, K~Cs) were obtained for a series of Ln(III) ions from La(III) to Lu(III) with exception of Ce(III) and Pm(III). These results show that the larger ionic radii of both lanthanide(III) and alkali metal ions make it feasible to form the M–Ln complexes. The formation of such complexes may prevent steric crowding around the Ln(III) and/or alkali metal ions.

Moreover, in the case of the benzylammonium complexes, the pure $BzNH_3-Pr^{III}$ and $BzNH_3-Eu^{III}$ complexes were obtained at the stoichiometric ratio of Ln(III) : (+)-tfbc of 1:4 but not of 1:3. On the other hand, the tetrakis((+)-hfbc) M^I or NH_4^+ –Ln(III) complexes were prepared in better yields at Ln(III) : (+)-tfbc of 1:3 than of 1:4. This suggests that the $BzNH_3^+$ has weaker affinity toward the fluorocarbons in (+)-hfbc than the M^I or NH_4^+ .

Attempts to synthesize tetrakis((+)-trifluoroacetylcamphorate) complexes having only a trifluoromethyl group in (+)-tfac, M^I $[Ln((+)-tfac)_4]$, failed by a similar preparation method to the present M–Ln complexes with a heptafluorobutyl group in (+)-hfbc. The larger number of the fluoromethylene substituents in (+)-hfbc[−] than that in (+)-tfa[−] plays an important role in forming the M–Ln complexes, since the M–Ln complexes could be stabilized by multidentate interaction of alkali metal ions with fluorine atoms in the fluorocarbons.

The thermogravimetry measurement of M^I $[Ln^{III}((+)-hfbc)_4] \cdot CH_3CN$ and M^I $[Ln^{III}((+)-hfbc)_4]H_2O$ gave 2.57% and 1.00% weight loss corresponding to one molar CH_3CN and H_2O , respectively. The drastic weight loss (about 78%) around 225–350 °C of the M–Ln complexes would be related with sublimation characteristics of tetrakis(β-diketonato) Ln(III) complexes such as $Cs[La(hfac)_4]$.²³

Circular Dichroism Spectra in the Intraligand $\pi-\pi^*$ Transitions

As shown in Figure 1, for crystals of the Na–Eu complex, a positive major solid diffuse reflectance CD component is observed in the intraligand $\pi-\pi^*$ transitions of (+)-hfbc[−] near 300 nm. This CD may result from the achiral configuration with mirror planes consisting of two mutually orthogonal trapezoids in the dodecahedron as found in the crystal structure of DD-8- $Na[Ln((+)-hfbc)_4] \cdot CH_3CN$ (Scheme 1).^{33,34} On the other hand, the Na–Ln complexes

in 2 mM CHCl₃ solution exhibit a negative CD couplet (a negative and a positive CD from longer to shorter wavelength) around 300 nm. This CD spectra are analogous in pattern and intensities to that for three helically bladed OC-6-Δ-[Si(acac)₃]⁺ having three β-diketonate(acac) long-axis π–π* transitions.³⁷ Thus, it is suggested in terms of the simple nonempirical exciton method on the basis of the interactions between the electric dipole moments in the helically arranged β-diketonate long-axis π–π* transitions that the Na–La complex in solution achieves a helically bladed SAPR-8-C₄(*III*)-Δ-configuration. Such a C₄ symmetry for the helically bladed SAPR-8 configuration is supported by the observation of the one set of the ¹⁹F-NMR signals^{33,34} of Na[La((+)-hfbc)₄]. Thus, the Na–Ln complexes are diastereoselectively formed in solution with helically four-bladed chiral Δ-SAPR-8-C₄(*III*) configuration with an encapsulated Na⁺ ion as shown in Figure 2. This is in agreement with the findings from other chiroptical techniques utilizing CPL^{31,35} and VCD³² as reported in the previous papers and also mentioned in the following sections.

Alkaline Metal Ions Dependence, Solvent Effect and Concentration Dependence of the Circular Dichroism

A series of CD couplet in the CD spectra of M^I[Ln((+)-hfbc)₄] in 0.02 mM CHCl₃ and 2 mM EtOH solutions shows the similar pattern with variation of alkali metal ion (Figs. 3, 4). CD intensities increase by two to three times in the order of Na⁺ < K⁺ < Rb⁺ < Cs⁺ with increasing alkaline metal ion radii. On the other hand, there is little difference in CD couplet intensity ratio (only by about 1.4 times) for the Cs–Ln across a series of Ln(III) ions (La, Nd, Eu, Yb, Fig. S1). This indicates that the M–Ln complexes are not dissociated into the alkali ion and Ln complexes in solutions as if it were ionic crystals where alkali metal ions play a role merely for the counter cation as seen in the intermolecular Cs[Y(hfac)₄] crystals.^{21,22} This means that the M–Ln complexes are a kind of molecular crystal where there is a fairly strong interaction of the fluorine atoms of the (+)-hfbc and the coordinated oxygen atoms around the lanthanide moiety with an alkali metal ion, resulting in the alkali metal ions dependence as mentioned in the succeeding paragraph.

In EtOH solution, there is remarkable concentration dependence as shown in Figures 4 and 5. In 2-mM solutions for the Na–La complex and in more dilute solutions (<2 mM) for the K–La (Figs. 4 and S2), there is no CD couplet but only a weak positive single CD band located at 305 nm with a shoulder at around 330 nm. On the other hand, a CD couplet is observed in 2-mM solutions for the K–La and in more concentrated EtOH solutions than 0.2 mM for the Rb–Ln and 0.1 mM for the Cs–Ln complexes (Fig. 6). The observation of these CD spectral features at various concentrations for the M–Ln systems suggests the presence of dissociated species. Additionally, the presence of a single positive CD component in the CD spectra of the dilute EtOH solutions of the M–Ln, which is similar to that for [Eu((+)-hfbc)₃] (Fig. S3), supports that [Eu((+)-hfbc)₃] would be a dissociated species in dilute EtOH solutions. We can observe that the intensity ratio, Δε(~300 nm)/Δε(~320 nm) of CD couplets in EtOH increases with decreasing the concentration as well as the alkali metal ions size. It is likely that this results from an increase in a positive band for [Eu((+)-hfbc)₃] and a decrease in the bisignate couplet for the M–Ln. Thus, the disappearance of the CD couplets suggests that the disruption of Δ-SAPR-8-Na[La((+)-hfbc)₄] occurs as substantiated by the excitation spectra of the ⁵D₀ ← ⁷F₀ Eu(III) transition. That is, two peaks were observed in the ⁵D₀ ← ⁷F₀ excitation spectra of the 2-mM Cs–Eu complex in EtOH solution (Fig. 7). The longer wavelength peak around 579.3 nm is coincident in position with that of [Eu((+)-hfbc)₃] in 2–0.2 mM EtOH solutions. Additionally, its peak area increases with decreasing the concentration from 2 to 0.2 mM EtOH solutions (Fig. 8). These results suggest that the dissociation equilibrium shifts toward [Ln((+)-hfbc)₃] and M((+)-hfbc) species from Δ-SAPR-8-M^I[Ln((+)-hfbc)₄] or that the degree of dissociation increases in the order of Na–La > K–La > Rb–La > Cs–La and also with decreasing the concentration. This agrees with the

fact that smaller alkali metal ions are more favorably solvated with EtOH than larger alkali metal ions.³⁸

The CD spectra of the Cs–Ln in CHCl₃ solution are also dependent on the concentration (Fig. 9). Since [Eu((+)-hfbc)₃] is very weakly emissive in CHCl₃, one of the two ⁵D₀ ← ⁷F₀ excitation peaks for the Cs–Eu complex in 2-mM CHCl₃ solution (Fig. 7) may not be necessarily assigned to [Eu((+)-hfbc)₃]. It may originate from a species with achiral DD-*D*_{2d}(*mmmm*)-8-Cs-Eu configuration as revealed by the X-ray structures of the Na–Ln complexes.^{32,33} Therefore, it is assumed that an equilibrium occurs in solution between the DD-8-M[La((+)-hfbc)₄] with achiral configuration and the configurationally chiral SAPR-8-M[La((+)-hfbc)₄]. The more dilute the concentration and the smaller the alkali metal ion size, the larger the CD couplets ratio, Δε(300 nm)/Δε(320 nm) and the less abundant SAPR-8-M[Ln((+)-hfbc)₄] are. This behavior is in accordance with the fact that a positive major peak observed in the solid CD spectrum of DD-8-Na-Eu (*vide supra*) increases and the bisignate couplet of SAPR-8-M-Ln complexes decreases.

The CD patterns and intensities in 2-mM EtOH solutions for the Cs–La, Rb–La, and K–La complexes are similar to those in 0.02-mM CHCl₃ solutions for the Cs–La, K–La, and Na–La complexes, respectively (Figs. 3, 4). This indicates that the M–Ln complexes in CHCl₃ solutions are much more inert or less dissociative than those in EtOH solutions.

In contrast to the CD results from CHCl₃ and EtOH solutions, the CD couplet for the M–La in CH₃CN solutions vary little with change of alkali metal ions (Fig. S4). In addition, the Cs–La complex in CH₃CN gives the smaller concentration dependence for the CD couplet with about half of the CD intensities as compared with those in 0.02-mM CHCl₃ and 2-mM EtOH solutions (Fig. 9). It is worth noting that such a CD behavior is parallel to the CPL pattern of the M–Eu.³⁵ The ratio of the luminescence dissymmetry factor, $g_{lum} = 2 (I_L - I_R)/(I_L + I_R)$, in the ⁵D₀–⁷F₁ emission for the Na–Eu versus Cs–Eu is approximately 1 vs. 2 in CH₃CN and approximately 1 vs. 6–10 in CHCl₃ and EtOH. (The magnitude of the g_{lum} value for the Cs–Eu in CH₃CN being about half of that for the Cs–Eu in CHCl₃ and EtOH.^{31,35}) This suggests that the change of the dissociation for the M–Ln complexes on decreasing with increasing the alkali metal ions size is smaller in CH₃CN solutions than in CHCl₃ and EtOH. This behavior is corroborated by observing two excitation peaks in the ⁵D₀ ← ⁷F₀ excitation spectrum of Cs–Eu in CH₃CN solution (Fig. 7). The longer wavelength peak is due to [Eu((+)-hfbc)₃] in CH₃CN that is more emissive than that in EtOH solutions.

The Exciton Circular Dichroism Spectra

In view of the alkali metal ions and concentration dependences of the CD couplets, it is clear that the difference in CD intensity with variation of alkali metal ions could result from the degree of dissociation and/or the amount of the SAPR-8-M-La complexes present in solution. Thus, it is difficult to make a straightforward evaluation for the accurate exciton CD intensities for each SAPR-8-M-La complex. Comparison of the CD couplets with the CPL and VCD makes it feasible to evaluate the relative ratio for the exciton CD intensities for the M–La complexes. The g_{lum} values for the CPL in CHCl₃ are not affected by the change of concentration, even if the SAPR-8-M-Eu complex is a minor species in dilute solutions and irrespective of the coexistence of the dissociated species.^{31,35} This shows that the ratio of the g_{lum} values for the genuine configurational chiral SAPR-8-M-Eu complexes is equal to 1.0:2.6:6.7:9.2 for Na–Eu : K–Eu : Rb–Eu : Cs–Eu. Therefore, the exciton CD intensity ratio is assumed to be close to the g_{lum} ratio for the CPL of the M–Eu complexes. On the other hand, the g_{VCD} value ratios for VCD couplets near 1550 cm^{−1} for the SAPR-8-M-La complexes in CDCl₃ solutions are 1.0:1.8:3.0:6.5 for Na–La : K–La : Rb–La : Cs–La with variation of alkali metal ion.³² Since the VCD measurements were carried out in more

concentrated solutions than 8 mM, one can assume that these solutions mostly contain the SAPR-8-M-Ln complexes. Thus, such a fairly large difference in ratio between the g_{lum} and g_{VCD} values would come from the difference in mechanism of chiroptical properties between CPL and VCD. The VCD couplets for the M-La complexes are interpreted in terms of the coupled oscillator model originating from the exciton interaction of the transition dipole moments for the C-C stretching in the β -diketonate chelate (*vide infra*). This model is the same physical formulation of the exciton CD in the π - π^* transition of the (+)-hfbc ligand. This is contrasted to the CPL in the $4f$ - $4f$ transitions that originate from the twist angle rotation of the ligating atoms in the first coordination shell from the regular cubic apex. Therefore, it is likely that the exciton CD intensity ratios for the M-La complexes are estimated to be in accordance with that for the VCD, i.e., 1.0:1.8:3.0:6.5 for Na-La : K-La : Rb-La : Cs-La rather than that for the CPL. The observed CD intensity ratios in 0.02-mM CHCl_3 solutions (1:2:3:4) for Na-La : K-La : Rb-La : Cs-La show a similar tendency to the earlier estimated one for the VCD. This is even if the existence of the achiral DD-8 species were taken into consideration. The exciton CD intensities for the SAPR-8-M-La complexes cannot be estimated accurately but would be estimated to be larger than the CD intensities (e.g., $\Delta\epsilon = +230$ at 300 nm and $-219 \text{ M}^{-1} \text{ cm}^{-1}$ at 328 nm for the Cs-La in 2-mM CHCl_3 solution). In addition, since the g_{lum} values of the CPL in EtOH for the M-Eu complexes are almost the same as those in CHCl_3 solution,³⁵ the exciton CD intensities for the SAPR-8-M-La complexes in EtOH and CHCl_3 solutions are similar to each other. Nevertheless, the observed CD couplets mimicking the exciton CD couplets are useable to determine the absolute configuration on the basis of the exciton model (*vide supra*).

In this context, for the ammonium and the benzylammonium complexes, $\text{NH}_4[\text{Ln}((+)\text{-hfbc})_4]$ and $\text{BzNH}_3[\text{Ln}((+)\text{-hfbc})_4]$, a negative CD couplet in CHCl_3 reflects that the exciton CD pattern would result from encapsulating NH_4^+ or BzNH_3^+ of which the protons interact with CF_2 in the heptafluorobutyl group, leading to forming a chiral Δ -SAPR-8 configuration.

A Description for the Chiral SAPR-8 Configuration

As mentioned previously, the alkali metal ions dependence of the exciton CD as shown in Figures 2 and 3 shows a similar tendency to that of the g_{lum} values for the CPL despite the difference in mechanism of chiroptical properties.³⁵ The semi-quantitative calculated rotational strengths based on the exciton coupling of the long-axis transition dipole moments of the β -diketonate chelates are proportional to $\sin 2\theta$ (θ is defined as the twist angle around the C_4 axis) in Δ -SAPR-8- C_4 -(*III*) configuration.² On the other hand, the rotational strength for the CPL and CD in the $4f$ - $4f$ transitions is proportional to $\sin 4\theta$ with the extreme at 22.5° for the twist angle rotation of the ligating atoms from the regular cubic apex as shown in Fig. S4. Experimentally, it is found that the exciton CD, VCD, and CPL exhibit the same tendency for the alkali metal ions dependence. Thus, the twist angle for the Cs-Ln complexes is estimated to be around 22.5° , and then, it decreases toward zero in the order of $\text{Rb-Ln} > \text{K-Ln} > \text{Na-Ln}$ with decreasing alkali metal ion size (Fig. S4). Such a geometrical change from Cs-La to Na-La is also inferred from a large difference in the $4f$ - $4f$ CD intensities between the Cs-Pr and Na-Pr complexes, probably due to a crystal field change.³⁴

It is interesting to note that the intensity ratio between the Na-La and Cs-La is much smaller (1:6.5) for the exciton CD and VCD³² than that (1:9.2) for the CPL.³⁵ This may reflect differences in mechanism of chiroptical properties resulting from the milder variation of $\sin 2\theta$ for the exciton CD and VCD than the rather steep one of $\sin 4\theta$ for CPL and $4f$ - $4f$ CD with change of the twist angles (θ) as in Fig. S4.

In view of the solvent effect as well as the alkali metal ions and concentration dependences mentioned earlier, it can be assumed that the encapsulation around the alkali metal ion by three C_3F_7 groups of $DD-8-M^I[Ln((+)-hfbc)_4] \cdot CH_3CN$ in crystals is more relaxed with lengthening the $M^+ \cdots F$ distance when it is dissolved in solution. That is, when Gutmann's bond length variation rule³⁹ is applied to the $(solvent \cdots F_1-C-F_2 \cdots M^+)$ moiety, the stronger the solvent $\cdots F_1$ interaction is, the longer the $F_2 \cdots M^+$ distance is. This is a result of lengthening the F_1-C bond and shortening the $C-F_2$ bond. In other words, the steric congestion around the encapsulated alkali metal ion is so relaxed that the four C_3F_7 groups are allowed to wrap the M^+ ion. Then, it is possible to form the SAPR-8- MLn (Fig. 2). The reason for the difference in solvent dependence of the CD behavior may be explained by the following consideration. The twist angle rotation around the C_4 axis could change the configurational chirality with increasing the solute-solvent interaction with variation of alkali metal ions. This is the case for the CD in $CHCl_3$ and EtOH. In CH_3CN , the weaker solute-solvent interaction leads to a less flexible configuration, resulting in little change of the CD with variation of alkali metal ions and concentrations. The fact that the CD intensities or configurational chirality in CH_3CN are smaller than those in $CHCl_3$ and EtOH may result from a weaker solvent-solute ($NCCH_3 \cdots FC$) interaction as inferred from the smaller acceptor number of CH_3CN (18.9) than those of $CHCl_3$ (23.1) and EtOH (37.1).⁴⁰

CONCLUSIONS

When the $M-Ln$ complexes are dissolved in solution, the $DD-8-M-Ln$ complex with achiral configuration partially turns to configurational chiral Δ -SAPR-8- $M-Ln$ complexes. The other part, however, remains as $DD-8-M-Ln$ in $CHCl_3$ or is dissociated into $[Ln((+)-hfbc)_3]$ and $M((+)-hfbc)$ in EtOH and CH_3CN . Therefore, the CD couplets in the $\pi-\pi^*$ transition of $(+)-hfbc$ ligand are not always compared with the exciton CD. They are given by summing the CD for an equilibrated mixture of the Δ -SAPR-8- $M-Ln$ complexes and the achiral configurational $DD-8-M-Ln$ or the dissociated $[Ln((+)-hfbc)_3]$ and $M((+)-hfbc)$.

Comparison in intensity between the CD and VCD or CPL for the Δ -SAPR-8- $M-Ln$ complexes makes it possible to evaluate the ratio of the exciton CD intensities among the $M-Ln$ complex. The observed CD couplet behavior mimics the exciton CD couplet and, also, reflects the difference in mechanism of chiroptical properties between the exciton or VCD spectra and the CPL or $4f-4f$ CD. This confirms the utility to determine the absolute configuration for $M-Ln$ complexes based on the CD couplets.

It is found that the $M-Ln$ complexes are diastereoselectively formed with chiral Δ -SAPR(C_4) configuration with four bidentate chelates retaining with aid of $M^+ \cdots FC$ interactions with an encapsulated alkali metal ion in solution. It is also so labile as to be disrupted owing to the solvation to F-C, where the stronger acceptor solvent or a smaller alkali metal ion accelerates the dissociation. Such a unique chiral stereochemistry is realized by combination of labile $Ln(III)$ complexes and weak $M^+ \cdots F-C$ interactions. The study on these types of complexes showing intense CD with variation of M^+ ions, solvents, or concentrations will be useful to provide important information on configurational chirality for chemical sensors, NMR shift reagents, or chiral catalysis.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

Contract grant sponsor: G.M. thanks the National Institute of Health, Minority Biomedical Research Support (1SC3 GM089589-03 and 3S06 GM008192-27S1) and the Henry Dreyfus Teacher-Scholar Award for financial support..

LITERATURE CITED

1. Aspinall HC. Chiral lanthanide complexes: coordination chemistry and applications. *Chem Rev.* 2002; 102:1807–1850. [PubMed: 12059255]
2. Bruce JI, Parker D, Lopinski S, Peacock RD. Survey of factors determining the circularly polarised luminescence of macrocyclic lanthanide complexes in solution. *Chirality.* 2002; 14:562–567. [PubMed: 12112329]
3. Bünzli JCG. Lanthanide luminescence for biomedical analyses and imaging. *Chem Rev.* 2010; 110:2729–2755. [PubMed: 20151630]
4. Di Bari L, Pescitelli G, Sherry AD, Woods M. Structural and chiroptical properties of the two coordination isomers of YbDOTA-type complexes. *Inorg Chem.* 2005; 44:8391–8398. [PubMed: 16270977]
5. Di Bari L, Salvadori P. Solution structure of chiral lanthanide complexes. *Coord Chem Rev.* 2005; 249:2854–2879.
6. Tsukube H, Shinoda S. Lanthanide complexes in molecular recognition and chirality sensing of biological substrates. *Chem Rev.* 2002; 102:2389–2403. [PubMed: 12059273]
7. Tsukube H, Shinoda S, Tamiaki H. Recognition and sensing of chiral biological substrates via lanthanide coordination chemistry. *Coord Chem Rev.* 2002; 226:227–234.
8. Gunnlaugsson T, Glynn M, Tocci GM, Kruger PE, Pfeffer FM. Anion recognition and sensing in organic and aqueous media using luminescent and colorimetric sensors. *Coord Chem Rev.* 2006; 250:3094–3117.
9. Montgomery CP, New EJ, Parker D, Peacock RD. Enantioselective regulation of a metal complex in reversible binding to serum albumin: dynamic helicity inversion signalled by circularly polarised luminescence. *Chem Commun.* 2008; 36:4261–4263.
10. Shinoda S, Tsukube H. Luminescent lanthanide complexes as analytical tools in anion sensing, pH indication and protein recognition. *Analyst.* 2011; 136:431–435. [PubMed: 21170445]
11. Di Bari L, Pintacuda G, Salvadori P. Stereochemistry and near-infrared circular dichroism of a chiral Yb complex. *J Am Chem Soc.* 2000; 122:5557–5562.
12. Di Bari L, Pintacuda G, Salvadori P. Stereoselection in the binding of Ln DOTA to γ -cyclodextrin: a near infrared circular dichroism study. *Chirality.* 2010; 22:E11–E16. [PubMed: 21038382]
13. Dickens RS, Howard JAK, Maupin CL, Moloney JM, Parker D, Peacock RD, Riehl JP, Siligardi G. Ground and excited state chiroptical properties of enantiopure macrocyclic tetranaphthyl lanthanide complexes: controlled modulation of the frequency and polarisation of emitted light. *New Jour Chem.* 1998; 22:891–899.
14. Cantuel M, Bernardinelli G, Imbert D, Bünzli JCG, Hopfgartner G, Piguet C. A kinetically inert and optically active CrIII partner in thermodynamically self-assembled heterodimetallic non-covalent d–f podates. *J Chem Soc Dalton Trans.* 2002; 9:1929–1940.
15. Cantuel M, Bernardinelli G, Muller G, Riehl JP, Piguet C. The first enantiomerically pure helical noncovalent tripod for assembling nine-coordinate lanthanide(III) podates. *Inorg Chem.* 2004; 43:1840–1849. [PubMed: 15018502]
16. Telfer SG, Tajima N, Kuroda R, Cantuel M, Piguet C. CD spectra of d–f heterobimetallic helicates with segmental di-imine ligands. *Inorg Chem.* 2004; 43:5302–5310. [PubMed: 15310208]
17. Petoud S, Muller G, Moore EG, Xu J, Sokolnicki J, Riehl JP, Le UN, Cohen SM, Raymond KN. Brilliant Sm, Eu, Tb, and Dy chiral lanthanide complexes with strong circularly polarized luminescence. *J Am Chem Soc.* 2007; 129:77–83. [PubMed: 17199285]
18. Tsukube H, Hosokubo M, Wada M, Shinoda S, Tamiaki H. Specific recognition of chiral amino alcohols via lanthanide coordination chemistry: structural optimization of lanthanide tris(β -diketonates) toward effective circular dichroism/fluorescence probing. *Inorg Chem.* 2001; 40:740–745. [PubMed: 11225117]
19. Nakanishi K, Dillon J. A simple method for determining the chirality of cyclic α -glycols with $\text{Pr}(\text{DPM})_3$ and $\text{Eu}(\text{DPM})_3$. *J Am Chem Soc.* 1971; 93:4058–4060.
20. Kepert D. Aspects of the stereochemistry of eight-coordination. *Prog Inorg Chem.* 1978; 24:179–249.

21. Bennett MJ, Cotton FA, Legzdins P, Lippard SJ. The crystal structure of cesium tetrakis(hexafluoroacetylacetonato)yttrate(III). A novel stereoisomer having dodecahedral eight-coordination. *Inorg Chem.* 1968; 7:1770–1776.
22. Lippard SJ, Cotton FA, Legzdins P. Geometry of the $[Y(CF_3COCHCOCF_3)_4]$ -ion. A new eight-coordinate stereoisomer in the dodecahedral class. *J Am Chem Soc.* 1966; 88:5930–5931.
23. Burns JH, Danford MD. The crystal structure of cesium tetrakis (hexafluoroacetylacetonato)europate and -americite. Isomorphism with the yttrate. *Inorg Chem.* 1969; 8:1780–1784.
24. Lalancette RA, Cefola M, Hamilton WC, La Placa SJ. Unusual dodecahedral coordination in the structure of ammonium tetrakis[4,4,4-trifluoro-1-(2-thienyl) 1,3-butanedione]praseodymate(III) monohydrate, $NH_4Pr(C_8H_4F_3O_2S)_4 \cdot H_2O$. *Inorg Chem.* 1967; 6:2127–2134.
25. Butman LA, Aslanov LA, Porai-Koshits MA. Crystal and molecular structure of acidic gadolinium tetrakisbenzoylacetate. *J Struct Chem.* 1970; 11:40–46.
26. Sweeting LM, Rheingold AL. Crystal disorder and triboluminescence: triethylammonium tetrakis(dibenzoylmethanato)europate. *J Am Chem Soc.* 1987; 109:2652–2658.
27. Muller G. Luminescent chiral lanthanide(III) complexes as potential molecular probes. *Dalton Trans.* 2009; 44:9692–9707. [PubMed: 19885510]
28. Brittain HG. Stereoselectivity in the adduct formation between chiral Eu(III) β -diketone complexes and sulfoxides, sulphones and phosphate esters. *Polyhedron.* 1983; 2:261–268.
29. Green TK, Whetstone JR, Son EJR. Enantiomeric purity of alkylmethylphenylsulfonium ions with chiral NMR shift reagents: racemization by pyramidal inversion as observed by 1H NMR spectroscopy. *Tetrahed Asymmet.* 1997; 8:3175–3181.
30. Harada T, Nakano Y, Fujiki M, Naito M, Kawai T, Hasegawa Y. Circularly polarized luminescence of Eu(III) complexes with point- and axis-chiral ligands dependent on coordination structures. *Inorg Chem.* 2009; 48:11242–11250. [PubMed: 19860395]
31. Lunkley JL, Shirotani D, Yamanari K, Kaizaki S, Muller G. Extraordinary circularly polarized luminescence activity exhibited by cesium tetrakis(3-heptafluorobutyryl-(+)-camphorato) Eu(III) complexes in EtOH and $CHCl_3$ solutions. *J Am Chem Soc.* 2008; 130:13814–13815. [PubMed: 18816117]
32. Sato H, Shirotani D, Yamanari K, Kaizaki S. Vibrational circular dichroism of Δ -SAPR-8-tetrakis[(+)-heptafluorobutyrylcamphorato]lanthanide(III) complexes with an encapsulated alkali metal ion. *Inorg Chem.* 2010; 49:356–358. [PubMed: 20000590]
33. Shirotani D, Suzuki T, Kaizaki S. Novel configurational structures of sodium tetrakis(3-heptafluorobutyryl-(+)-camphorato) Ln(III) complexes with a trapped Na^+ by $Na^+ \cdots FC$ interactions in the solid state and in solution. *Inorg Chem.* 2006; 45:6111–6113. [PubMed: 16878913]
34. Shirotani D, Suzuki T, Yamanari K, Kaizaki S. Crystal structure and chiroptical spectra of sodium tetrakis (+)-hfbc Pr(III) complex. *J Alloy and Comp.* 2008; 451:325–328.
35. Lunkley JL, Shirotani D, Yamanari K, Kaizaki S, Muller G. Chiroptical spectra of a series of tetrakis[(+)-3-heptafluorobutyrylcamphorato]lanthanide(III) with an encapsulated alkali metal ion: circularly polarized luminescence and absolute chiral structures for the Eu(III) and Sm(III) complexes. *Inorg Chem.* 2011; 50:12724–12732. [PubMed: 22074461]
36. Richardson MF, Wagner WF, Sands DE. Rare-earth trisheptafluoroacetylacetonates and related compounds. *J Inorg Nucl Chem.* 1968; 30:1275–1289.
37. Larsen E, Mason SF, Searle GH. The absorption and the circular dichroism spectra and the absolute configuration of the tris acetylacetonato silicon(IV) ion. *Acta Chim Scand.* 1966; 20:191–196.
38. Lahiri SC. Determination of Gibbs energies of solvation of monovalent ions in water, methanol and ethanol and re-evaluation of the interaction energies. *Zeitschrift fur Physik Chemie.* 2003; 217:13–33.
39. Gutmann V, Resch G, Linert W. Structural variability in solutions. *Coord Chem Rev.* 1982; 43:133–164.
40. Mayer U, Gutmann V, Gerger W. The acceptor number - a quantitative empirical parameter for the electrophilic properties of solvents. *Monatsh Chemie.* 1975; 106:1235–1257.

Fig. 1. (a) Solid diffuse reflectance circular dichroism (right ordinate) and (b) circular dichroism couplet in CHCl_3 (left ordinate) of the Na–Eu complex $\text{Na}[\text{Eu}(+)\text{-hfbc}_4] \cdot \text{CH}_3\text{CN}$ in the ultraviolet region.

Fig. 2.
Proposed solution structure of Δ -SAPR-8-M-Ln complex.

Fig. 3.
Circular dichroism couplets of $M^I[\text{La}((+)\text{-hfbc})_4]$ in 0.02-mM CHCl_3 . Cs-La (red), Rb-La (blue), K-La (green), and Na-La (black).

Fig. 4. Circular dichroism of $\text{M}^{\text{I}}[\text{La}((+)\text{-hfbc})_4]$ in 2-mM EtOH. Cs-La (red), Rb-La (blue), K-La (green), and Na-La (black).

Fig. 5. Concentration-dependent circular dichroism of $\text{M}^{\text{I}}[\text{La}((+)\text{-hfbc})_4]$ (a) Na-La and (b) K-La in EtOH: 0.02 mM (green), 0.2 mM (blue), and 2 mM (red).

Fig. 6. Concentration-dependent circular dichroism of $M^I[La((+)\text{-hfbc})_4]$ (a) Rb-La and (b) Cs-La in EtOH: 0.2 mM (red), 0.1 mM (blue), 0.05 mM (green), and 0.02 mM (black).

Fig. 7. Excitation spectra of the $^5D_0 \leftarrow ^7F_0$ transition of the Cs-Eu complex in 2-mM CHCl₃ (left), EtOH (middle), and CH₃CN (right) at 295 K, upon monitoring at about 612 nm, respectively.

Fig. 8. Excitation spectra of the $^5D_0 \leftarrow ^7F_0$ transition of the Cs-Eu (solid lines) and [Eu((+)-hfbc)₃] (medium dashes) in 2 mM (black), 0.5 mM (blue), and 0.2 mM EtOH (red) at 295 K, upon monitoring at about 612 nm, respectively.

Fig. 9. Circular dichroism couplet of the Cs–La in 2 mM (solid line) and 0.02 mM (dashed line) of CHCl_3 (blue) and CH_3CN (red).

(a) $DD-D_{2d}(mmmm)-8$

(b) $DD-D_2(gggg)-8$

(c) $SAPR-D_2(ssss)-8$

(d) $SAPR-D_4(IIII)-8$

Scheme 1.

Eight coordinate stereochemistry of tetrakis(bidentate) complexes.

Scheme 2.
Chiral camphorate β -diketonato ligand.