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Vibrational Circular Dichroism of Δ-SAPR-8-tetrakis[(+)-heptafluorobutyrylcamphorato]lanthanide(III) Complexes with an Encapsulated Alkali Metal Ion

Hisako Sato,*[†,‡] Dai Shirotani,[§] Kazuaki Yamanari,[§] and Sumio Kaizaki*[⊥]

[†]*Department of Chemistry, Faculty of Science, Ehime University, Matsuyama, Ehime 790-8577, Japan,* [‡]*PRESTO, Japan Science and Technology Agency, Tokyo, Japan,* [§]*Institute for Higher Education Research and Practice, Osaka University, Toyonaka, Osaka 560-0043, Japan, and* [⊥]*Center for Advanced Science and Innovation, Osaka University, Suita, Osaka 565-0871, Japan*

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The vibrational circular dichroism (VCD) spectra for Δ-M[Ln((+)-hfbc)$_4$] (M^{I} = Na, K, Rb, Cs; Ln^{III} = La, Eu; abbreviated as M−Ln) and Δ-Cs[Yb((+)-hfbc)$_4$] (Cs−Yb) were observed in $CDCl_3$ solutions. The VCD signs and/or intensities are mostly different from those of the Δ-tris(β-diketonato) transition-metal complexes. The M−Ln complexes give the strong VCD peak(s) near 1550 cm^{-1}. These VCD patterns are different from each lanthanide(III) complex, but their intensities change with variation of the alkali metal ion. A positive−negative couplet VCD near 1550 cm^{-1} for the Δ-M−La complexes is observed similarly for the Δ-tris(β-diketonato) complexes, confirming the assignment to the Δ absolute configuration based on the exciton CD. The density functional theory calculated VCD for the two peaks at 1650 and 1550 cm^{-1} reproduces the relative intensity and signs of the observed ones for the Δ-M−La^{III} complexes.

Vibrational circular dichroism (VCD) spectra measure the difference in the absorption intensity for right versus left circularly polarized light in the IR region. VCD spectra have been applied to transition-metal complexes as a potential tool for determining chiral absolute structures since the pioneering works on the VCD spectra of [Co(acac)$_2$(L-alaninato)][1] or related complexes[2] by Nafie et al. Of special interest is the importance of using VCD for studying only vicinal ligand vibrations localized in the systems of interest, in contrast to electronic circular dichroism (ECD), which is influenced by most chromophores in metal complexes. The recent studies on VCD spectra of metal complexes have demonstrated two characteristic properties that depend on the central metal ion. One is the influence of the d electron configurations of central transition-metal ions for tris(β-diketonato) metal complexes on the VCD as revealed by Sato et al.'s experimental and density functional theory (DFT) calculation studies.[3,4] The other is the effect of the low-lying excited electronic states (LLESs) on the enhancement of VCD in transition-metal complexes as claimed by Nafie et al.[5−8] The first hint for the LLES study on (+)-camphorato-type complexes was the difference in the VCD spectra between tris[trifluoromethylhydroxymethylene-(+)-camphorato]praseodymium(III) and -europium(III) complexes, of which the chiral structures were not determined.[5,6] So far, there have been no studies on the VCD spectra of lanthanide(III) complexes with determined chiral structures. We reported on the isolation and structural characterization of sodium or cesium tetrakis[3-heptafluorobutylryl-(+)-camphorato]lanthanide(III) complexes, M^{I}[Ln((+)-hfbc)$_4$] (Scheme 1), by X-ray analysis and/or chiroptical spectroscopy [ECD[9] and circularly polarized luminescence (CPL)].[10] It has been found that the solution structure is formed stereospecifically to take a Δ absolute configuration of square-antiprism eight-coordinate (SAPR-8), four-bladed D_4(*llll*) (*l* between sites in different squares) structure on the basis of the exciton ECD spectra and ^{19}F NMR, in contrast to the pseudo achiral D_{2d} configuration in the solid state.[9] Therefore, it is invaluable to

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*To whom correspondence should be addressed. E-mail: kaizaki@chem.sci.osaka-u.ac.jp.

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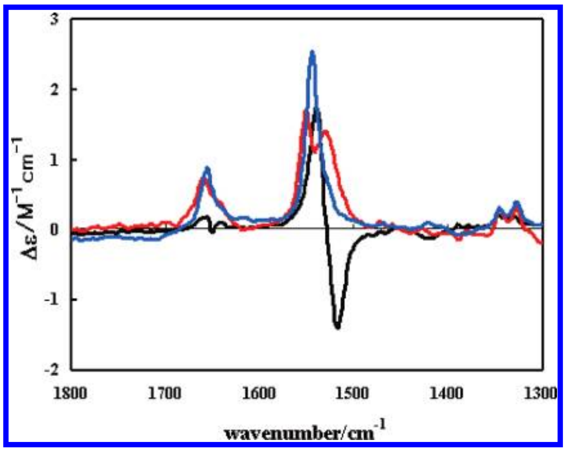
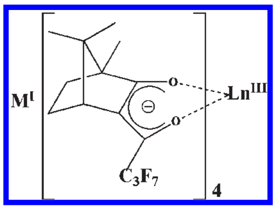


Figure 1. Observed VCD spectra of Cs[Ln((+)hfbc)$_4$] in CDCl$_3$. Ln = black (La), blue (Eu), and red (Yb).

Scheme 1. $M^I[Ln^{III}((+)\text{-hfbc})_4]$



examine any affect on VCD with variation of central lanthanide ions and/or alkali metal ions in comparison with tris(β-diketonato) transition-metal complexes because chiral polyhedral stereochemistry of lanthanide complexes is a fundamental information for lanthanide ion recognition and chiral sensing of biological substances.[11]

In this Communication, the VCD spectra of $M^I[Ln((+)\text{-hfbc})_4]$ complexes (Ln^{III} = La, Eu, or Yb; M^I = Na, K, Rb, and Cs) in CDCl$_3$ were examined as compared with the DFT calculation as well as ECD and/or CPL.

The $M^I[Ln((+)\text{-hfbc})_4]\cdot CH_3CN$ or H_2O (Ln^{III} = La, Eu, and Yb; M^I = Na, K, Rb, and Cs) complexes were obtained as crystals by reported methods.[9] The IR spectra of M[Ln((+)-hfbc)$_4$] in CDCl$_3$ are similar to each other and analogous to those of [M(acac)$_3$] (Figure S1 in the Supporting Information). As shown in Figure 1, the Cs−Ln complexes give a positive VCD peak at 1655 cm^{-1} and a strong peak(s) at 1550 cm^{-1}, respectively, probably corresponding to the VCD peaks observed at 1650−1550 cm^{-1} for the C−O stretching and 1550−1450 cm^{-1} for the C−C stretching of Δ-[M(β-diketonato)$_3$],[1,3,4] although the former 1655 cm^{-1} peak for the Cs−La complex could not be observed. The Cs−La^{III} complex gives a strong positive−negative VCD couplet around 1550 cm^{-1} as observed for Δ-[M(β-diketonato)$_3$],[1,3,4] while a positive single peak for the Cs−Eu^{III} complex and two positive peaks for the Cs−Yb^{III} complex are observed. These VCD intensities of the Cs−Ln^{III} complexes are similar to each other and, hence, are little affected by the kinds of the central lanthanide ions as inferred from the exciton ECD spectra.[9] However, these intensities are larger by several times than the corresponding ones of Δ-[M(β-diketonato)$_3$].[1,3,4] Although Eu^{III} complexes have a low-lying $^7F_1$ excited state above 360 cm^{-1} from the lowest-lying $^7F_0$ ground state, the VCD intensities for the Cs−Eu complex are not enhanced. Thus, the difference in the VCD patterns of the M−Eu complexes from the other M−Ln complexes may not be due to the LLES. For the M−Eu and Cs−Yb complexes, however, it is not clear whether the positive VCD peak(s) around 1550 cm^{-1} is due to the f electron configuration or the difference between the diamagnetic properties for the M−La complexes and the paramagnetic properties for the M−Eu and Cs−Yb complexes so far.

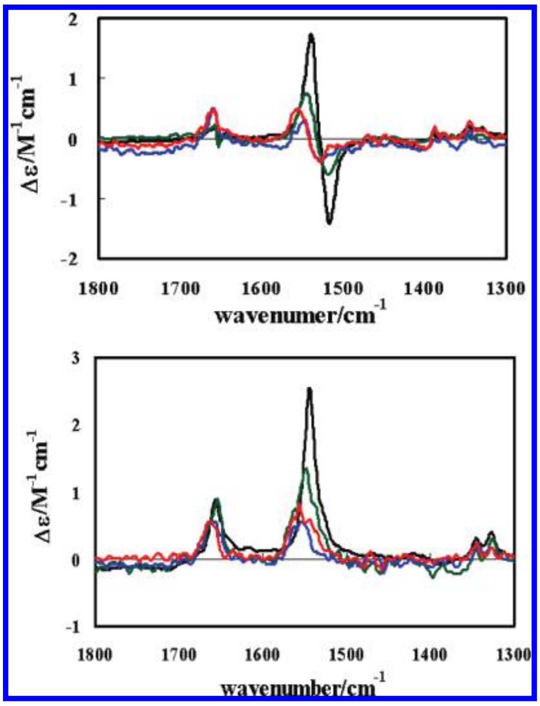


Figure 2. Observed VCD of M[Ln((+)-hfbc)$_4$] in CDCl$_3$. Ln = La (upper) and Eu (lower); M = Na (red), K (blue), Rb (green), and Cs (black).

For two series of the M−La^{III} and M−Eu^{III} complexes, the VCD intensities increase in the order of K < Rb < Cs except the Na−Ln complexes (Figure 2) as was similarly observed for the exciton ECD[9] and CPL spectra.[10] These chiroptical behaviors seem to reflect the variation of twist angles around the C_4 axis in the helically four-bladed $C_4(llll)$ chiral configuration with a change of the encapsulated alkali metal ion radii. On the other hand, the VCD intensity of the single positive peak around 1650 cm^{-1} changes irregularly with variation of the alkali metal ion radii, as in Figure 2. This fact suggests that the VCD activity of the positive peak does not always respond to the helical disposition of the four chelates, in contrast to the VCD peaks around 1550 cm^{-1}.

In order to theoretically calculate the VCD spectra for the M−Ln^{III} complexes, the structure optimization was performed for the simplified model of tetrakis(β-diketonato)lanthanide(III) complexes by use of the *Gaussian 03* program at the DFT level. There are two configurations for SAPR-8 tetrakis(didentate chelate) complexes[12]: one is found most frequently as $D_2(ssss)$ (s between sites in the same square) or distorted DD-8[13] and the other only one for

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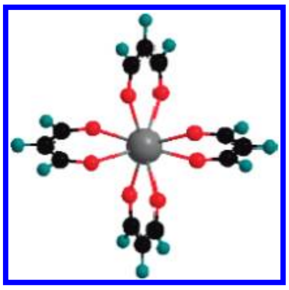
Scheme 2. $[La(malon)_4]^-$



SAPR-8-D_4(*llll*)-$[Nb^{IV}(dmp_4)]$ (dmp = 2,2,6,6-tetramethyl-3,5-heptanedionate) with four helically bladed propellers.[14] The present M−Ln complexes are confirmed to take a D_4 or C_4(*llll*) configuration by observing[10] the single $^5D_0-^7F_2$ emission peak[15] of the $M-Eu^{III}$ complexes as well as the exciton ECD and ^{19}F NMR spectra (Figure S3 in the Supporting Information).[9] The proposed D_4(*llll*) configuration was successfully optimized only for the most simplified model complex $[La(malon)_4]^-$ (Hmalon = malonaldehyde; Scheme 2) but not for the corresponding Eu and Yb complexes and the seemingly more realistic model $[La(acac)_4]^-$. This optimized result supports the fact that the chiral Δ-SAPR-(C_4) configuration is stereospecifically formed with the aid of $M^I\cdots$fluorocarbon (FC) interactions as evidenced from X-ray analysis;[9] otherwise, the D_2(*ssss*) configuration would be stabilized in view of steric hindrance, as found for most tetrakis(β-diketonato)lanthanide(III) complexes.[12,13]

The calculated IR and VCD spectra for $[La(malon)_4]^-$ are shown in Figure 3. The calculated result of the Δ isomer reproduces the observed one for the $M-La^{III}$ complexes except the higher frequency shift of the peak positions. A weak positive calculated peak at 1709 cm^{-1} and a positive−negative calculated couplet around 1580 cm^{-1} are assigned, respectively, to the C−O stretching and the combined mode of the C−O and C−C stretchings in accordance with those for Δ-$[M(\beta\text{-diketonato})_3]$ as mentioned above.[1,3,4] Thus, the calculated single peak and couplet correspond to a positive single peak at 1659 cm^{-1} and a positive−negative couplet around 1550 cm^{-1} observed for the M−La complexes, respectively. The observation of a positive−negative couplet around 1550 cm^{-1} leads to the assignment of the Δ absolute configuration of M[La((+)-hfbc)$_4$] according to the coupled oscillator model as applied to the VCD couplet around 1520 cm^{-1} for the C−C stretching of Δ-$[Co(acac)_3]$.[1] This result agrees with the absolute configuration based on the exciton ECD.[9] A positive single VCD sign at 1659 cm^{-1} of Δ-M−La complexes is opposite to the negative sign found for Δ-$[M(\beta\text{-diketonato})_3]$.[1,3,4] A positive−negative calculated couplet around 1400 cm^{-1} for the C−O stretching may be due to an observed IR peak around 1350 cm^{-1}. As shown in Figures 2 and 3, however, it is noted that the VCD around 1350 cm^{-1} could not be observed, in contrast to strong VCD couplets around 1450−1350 cm^{-1} for the C−O stretching of Δ-$[M(\beta\text{-diketonato})_3]$, which demonstrates the influence of the d electron configuration of the central metal ion.[3]

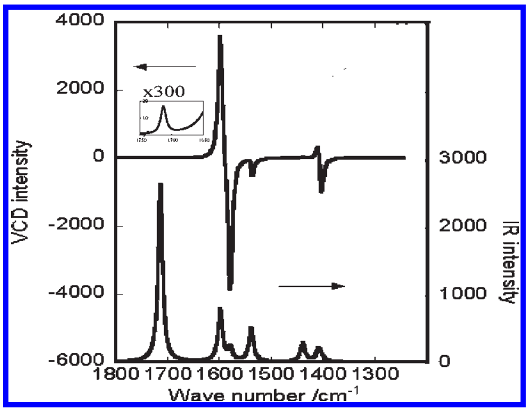


Figure 3. Calculated IR (lower) and VCD (upper) of Δ-$[La(malon)_4]^-$. No correction of the introduction of a scale factor was made for these spectra.

In summary, the VCD spectra for the M−Ln complexes are mostly different in patterns and signs from those of Δ-$[M(\beta\text{-diketonato})_3]$. The strong VCD peaks observed near 1550 cm^{-1} are different in pattern with variation of the central lanthanide(III) ions. Like the exciton ECD spectra, this VCD becomes stronger in the order of K < Rb < Cs, whereas the VCD intensities are little affected by the kinds of the lanthanide ions. The LLES does not affect the VCD for the $M-Eu^{III}$ complexes. The DFT calculated VCD reproduces the relative intensity and signs of the observed VCD patterns at 1650 and 1550 cm^{-1} for the Δ-$M-La^{III}$ complexes. The positive−negative VCD couplet of the M−La complexes together with the structure optimization by the DFT calculation supports the stereospecific formation of chiral Δ-SAPR-(C_4(*llll*)) configurations with the aid of $CF\cdots M$ intramolecular interaction. The present new information on VCD provides potential probes to reveal the configurational chirality of lanthanide complexes.

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Supporting Information Available: Experimental and theoretical details, IR spectra of M−La, M−Eu, and Cs−Yb complexes in $CDCl_3$ (Figure S1), VCD spectra of Cs[Eu((+)-hfbc)$_4$] and Cs[Eu((+)-hfbc)$_4$] (Figure S2), and ^{19}F NMR of Na[La((+)-hfbc)$_4$]$\cdot CH_3CN$ (Figure S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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