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Communication

Novel Configurational Structures of Sodium Tetrakis(3-heptafluorobutylryl-($+$)-camphorato) Ln(III) Complexes with a Trapped Na$^+$ by Na$^+$···FC Interactions in the Solid State and in Solution

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For newly prepared sodium tetrakis(3-heptafluorobutylryl-(+)-camphorato) Ln(III) complexes, the X-ray crystal analysis revealed an unprecedented pseudo-achiral dodecahedron (DD-8 (D_{2d})), whereas in CHCl$_3$ solution, the exciton CD and ^{19}F NMR spectra showed a novel chiral Δ-SAPR-8 (C_4) configuration which is stereospecifically formed by a trapped Na$^+$ ion with Na$^+$···FC (fluorocarbon) interactions.

Recently, much attention has been paid to lanthanide complexes from the viewpoint of luminescence as light sources or chemical sensing, biological applications or chiral catalysis, and molecular magnetism.[1−5] Configurational chirality of polyhedral stereochemistry around the Ln ion provides fundamental information to reveal lanthanide ion recognition and chiral sensing of biological substrates on the basis of specific spectra−structure relationships in view of the lability or Ln ion size and coordination number.[1−4] Chiral macrocyclic tetramine tetracarboxylate octadentate ligands 'dota'[6,7] or helical noncovalent d−f tripodes[8a−c] or terdentate chiral ligands[8d] result in diastereoselective formation of
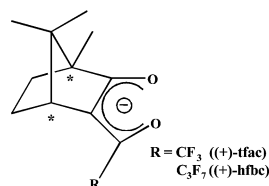
structurally robust configurational chiral lanthanide complexes, even in solution. We have studied the 3d−4f heterometal dinuclear complexes where the steric control around labile lanthanide ions was realized by intramolecular interactions.[9,10] Afterward, unique stereospecific consequences in the tetrakis(μ-(S)-phenylbutylato-k^2O) dinuclear Ln−Ln complexes were found through weak Ln···O interactions between one Ln ion and the coordinated oxygen at the other Ln ion.[11] On the other hand, the chiral β-diketonate didentate ligands such as (+)-hfbc(3-heptafluorobutylryl-(+)-camphorate) or (+)-tfac(3-trifluoroacetyl-(+)-camphorate) (Chart 1) give labile Ln complexes of which the solution structures were not well characterized,[12,13] although [Eu((+)-hfbc or -tfac)$_3$] has been extensively utilized for chiral discrimination by NMR or circular dichroism (CD). There has been no study on [Ln((+)-hfbc)$_4$]$^-$, which is expected to take a stereospecifical chiral configuration, owing to bulky steric requirement as suggested for [Eu((+)-hfbc or (+)-tfac)$_3$(dmso)] by the CPL study[12] and unidentified [Eu((+)-tfac)$_4$]$^-$ used for NMR shift reagents.[13] X-ray structures of Cs[Ln(hfac)$_4$](Ln = Eu,Y) demonstrated that they take a dodecahedral (DD) configuration with intermolecular Cs$^+$···FC (fluorocarbon) interactions.[14] The alkaline metal cation···FC interactions in many metal−fluorocarbon complexes have been interested in coordination chemistry of CF units.[15]

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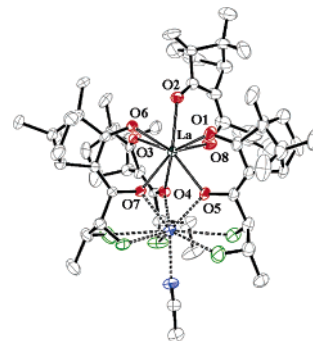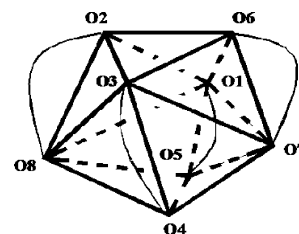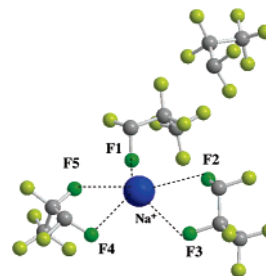
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Chart 1

R = CF$_3$ ((+)-tfac)
C$_3$F$_7$ ((+)-hfbc)

The present paper will report structural characterization of Na[La((+)-hfbc)$_4$]·CH$_3$CN in both the solid state and in solution with respect to configurational chirality. The tetrakis-((+)-hfbc) Ln complexes were synthesized by the modified method for [Ln(hfac)$_3$][16] with use of CHCl$_3$ and Et$_3$N[17] instead of ether and aqueous ammonia. The reaction condition for the preparation of Na[Ln((+)-hfbc)$_4$] is remarkable in view of a mole ratio of [Ln^{III}]/[(+)-hfbc$^-$] = 1:3 in the reaction mixture, as well as a source of Na$^+$ originating from desiccant anhydrous Na$_2$SO$_4$, which is insoluble in chloroform. Thus, the four C$_3$F$_7$ groups may play an important role to form Na[Ln((+)-hfbc)$_4$]. The X-ray crystal structural analysis[18] is the first one among mononuclear homoleptic tris- or tetrakis(chiral β-diketonato) complexes, [Ln((+)-hfbc or -tfac)$_n$]$^{n-3}$ (n = 3 or 4), though the heteroleptic dinuclear [Pr$_2$((+)-tfac)$_6$(dmf)$_3$] with a monocapped square antiprisim has been reported.[19] The ORTEP drawing of Na[La((+)-hfbc)$_4$]·CH$_3$CN is shown in Figure 1. Eight oxygen atoms of four (+)-hfbc ligands are eight-coordinated around La^{III} with Ln–O bond lengths ranging from 2.409(12) to 2.536-(8) Å. This complex exhibits a distorted DD (Figure 2) like Cs[Ln(hfac)$_4$],[14] according to the polyhedral analysis.[20]

However, the whole coordination geometry is unprecedented in view of configurational chirality. That is, two sets of four oxygens, (O1, O3, O4, O5) and (O2, O6, O7, O8), form two trapezoids lying mutually orthogonal mirror planes; a pair of two (+)-hfbc$^-$ chelates is disposed symmetrically with respect to the mirror planes (Figure 2). Accordingly,

Figure 1. ORTEP structure of Na[La((+)-hfbc)$_4$]·CH$_3$CN.

Figure 2. DD-8(D_{2h}) configuration of [La((+)-hfbc)$_4$]$^-$.

Figure 3. Na$^+$···FC interactions (broken lines) by three C$_3$F$_7$ groups of (+)-hfbc. Upper right shows the dangling C$_3$F$_7$ group.

for Na[La((+)-hfbc)$_4$]·CH$_3$CN, only one diastereomer or pseudo-enatiomer is nondiastereoselectivly formed with a "pseudo achiral DD(D_{2d}) configuration" around the La ion. This is in contrast to the related configurationally chiral DD-8(D_2)-Cs[Ln(hfac)$_4$][14] and SAPR-8(D_2)-(Et$_3$NH)[Eu(dbm)$_4$].[21] Such a pseudo-achiral configuration surrounded by four chiral ligands may be brought about by the Na$^+$···O–La and/or Na$^+$···FC interactions(vide infra) as inferred from the recent reports on the formation of the similar distorted DD-8(D_{2d}) {K[Yb(tropolonato)$_4$]·dmf}$_\infty$ with K···O–Yb interaction[22] and a diastereomeric pair of SAPR-8(D_2)-[Nd((+)-hfbc)$_3$(IM2py)](imino nitroxide radical IM2py = 2(2′-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-ox-yl).[23]

In an ion pair formed by the complex anion and sodium cation, Na$^+$ is surrounded by one nitrogen of CH$_3$CN, three oxygen atoms (O4, O5, O7) coordinated to the La ion with each Na$^+$···O–La distance within 2.374(10)−2.450(10) Å, and five fluorine atoms of C$_3$F$_7$ groups of the (+)-hfbc$^-$ ligands with the Na$^+$···FC interactions, as shown in Figure 3. Three of four C$_3$F$_7$ groups are involved in the Na$^+$···FC interactions, and the remaining C$_3$F$_7$ group is dangling. As

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(17) (a) LaCl$_3$·7H$_2$O (0.32 mmol) was dissolved in water (15 mL), and 0.96 mmol of (+)-Hhfbc was deprotonated by Et$_3$N in chloroform (30 mL). These two solutions were mixed in a separatory funnel by shaking. To the separated chloroform layer was added an excess amount of Na$_2$SO$_4$ in order to dry the solution. After filtration, this solution was concentrated to dryness. Then, a white powder was obtained. This powder was dissolved in acetonitrile (35 mL). After the solution was left for several days, plate crystals were obtained. Yield 9%. Anal. Calcd for C$_{58}$H$_{59}$NO$_8$F$_{28}$LaNa(Na[La((+)-hfbc)$_4$]·CH$_3$CN): C, 43.76; H, 3.74; N, 0.88%. Found: C, 43.63; H, 3.65; N, 0.93%. (b) For the Cs complexes, the preparative procedure is the same except that CsCl aqueous solution was used instead of Na$_2$SO$_4$. The fine needles obtained were identified as Cs[Ln((+)-hfbc)$_4$]·H$_2$O for La, Pr, and Yb by elemental analysis.
(18) The X-ray analysis was carried out on a Rigaku AFC7R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) at 296 ± 1 K. C$_{58}$H$_{59}$NO$_8$F$_{28}$LaNa, orthorhombic, $P2_1P2_1P2_1$ (No. 19), Z = 4. M_r = 1591.96 g/mol, a = 21.187(6) Å, b = 24.286(5) Å, c = 13.220(5) Å, α = β = γ = 90.00°, V = 6803(3) Å^3. 8539 reflections measured, 8503 unique used in all calculations. Final R1 = 0.0486. CCDC 265610 contains the supplementary crystallographic data for this paper.
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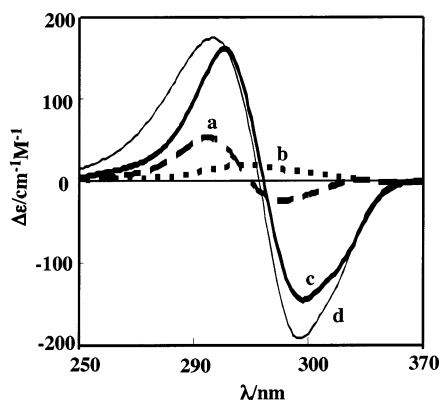
Figure 4. CD spectra: (a) the Na−La (···) in CHCl₃ and (b) (−) in EtOlH, (c) the Cs−La (—), and Cs−Yb (−) in CHCl₃.

Figure 5. Proposed structure in solution of Δ-M^I[Ln((+)-hfbc)₄]; side view (left) and top view (right).

for the Na^+···FC interactions, one C_3F_7 group is monodentate (F1) at the α-CF₂ and the other two C_3F_7 groups coordinate as didentate ligands (F2 and F3; F4 and F5) at each CF_2–CF_2. Each Na^+···FC distance is in the range 2.684(12)− 2.967(13) Å, which is close to the literature values,[15] much shorter than the van der Waals contacts (Na···F_{VDW} = 3.80 Å). The Na^+···FC interactions, as well as Na^+···O−La one in the ion pair, are an intramolecular mode, forming a discrete ion pair or a kind of Na−La or 3s−4f dinuclear complex with the chemical formula like [La{((+)-hfbc)₃Na}((+)-hfbc)]. This leads to the molecular crystal but not the ionic crystal, in contrast to the intermolecular mode in Cs[Ln-(hfac)₄].[14] This difference would result from the greater number of fluorine atoms at the substitution group in (+)-hfbc⁻ than that in hfac⁻. It is noted that the bulkier camphore groups are located at the one side in such a way that there would occur severe steric hindrance, resulting from the grasp of three less bulky C_3F_7 groups in (+)-hfbc⁻ by Na^+ ion at the other side. Such a steric disadvantage could be overcome by stabilizing the unique configuration with the Na^+···FC and/or Na^+···O−La interactions. For the corresponding Nd and Pr complexes, the crystals were also found to be isomorphous with the La complex and their X-ray strucutres are almost the same as the La complex.

CD measurements of the Na−Ln(La, Pr, Nd) complex in CHCl₃ exhibit a strong couplet around 310 nm, as shown in Figure 4. This is a typical pattern of the exciton CD band arising from the coupling between the long-axis π−π* transition dipole moments of (+)-hfbc with the helical disposition.[6b,8c,24] The molar CD intensity $\Delta\epsilon$ of the Na−La complex is similar to those of the other Na−Ln complexes and close to those observed for the exciton CD of [Si(acac)₃]⁺ and [Si((+)-hmc or (+)-atc)₃]⁺.[24] This indicates the con-figurational chirality around the central Ln ion in CHCl₃ in contrast to the solid structure. In ethanol, a single positive weaker CD of the Na−La complex is observed (Figure 4), evidencing the disruption of the configurational chirality owing to the stronger solvation of ethanol with Na^+. The corresponding Cs−Ln complexes, Cs[Ln((+)-hfbc)₄]·H₂O (Ln = La, Pr, and Yb),[17b] give much larger exciton CD couplets than the Na−Ln complexes. However, the difference
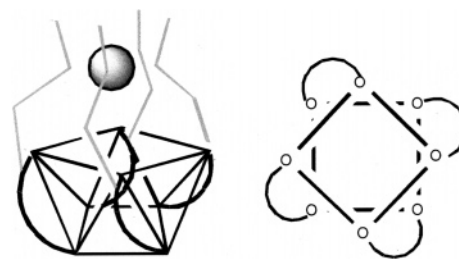
in CD intensities between the Cs−La and Cs−Yb complex with the largest and smallest Ln ion radii, respectively, are very small (Figure 4). These facts indicate that the chiral configuration or helicity is affected by the alkaline metal ion sizes but not by the Ln ion sizes. Moreover, the CD intensity ($\Delta\epsilon$ = −1.2) in the NIR $^2F_{7/2}$−$^2F_{5/2}$ 4f−4f transition of the Cs−Yb complex is much larger than those(< −0.8) for the reported Yb complexes.[7b−d,9a] The absolute config-uration of the three Yb complexes with a negative CD peak is in accordance with the Δ configuration on the basis of the exciton theory.[8c,24] ^{19}F NMR spectra of the Na− and Cs−La complexes in CDCl₃ show only one set of signals, probably due to four equivalent (+)-hfbc ligands unlike two kinds of inequivalent ones in the solid. The quartet of quartets near −35 ppm for the β-CF₂ and doublet of doublets at −50 ppm for the α-CF₂ of ^{19}F NMR are due to the inequivalent fluorine of the β-CF₂ (Figure S1). This suggests the mono-dentate coordination at the β-CF₂ of the four C_3F_7 groups. Accordingly, it is evident that the helical Δ-SAPR-8(C₄) arrangement of the four (+)-hfbc chelates in CHCl₃ accounts for the CD and NMR patterns of the M^I−Ln complexes formulated like [Ln{((+)-hfbc)₄M^I}], as shown in Figure 5. The exciton CD spectra are the first observation of the tetrakis(bidentate) Ln(III) complexes, though two exciton CD examples were reported for the robust mono(octadentate) DOTA Ln(III) complexes[6a,b] and the tris(tridentate) Ln(III) complexes with a kinetically inert chiral Cr(III) unit.[7c]

In conclusion, the stereospecifically formed chiral Δ-SAPR-(C₄) configuration with four didentate chelates is first found to be retained with aid of Na^+···FC interactions with a trap-ped sodium ion even in CHCl₃ , but it is so labile as to be disrupted in ethanol, owing to the solvation to Na^+. Such an unique chiral stereochemistry is realized by combination of labile Ln complexes and weak Na^+···F−C interactions. The study on this type of complex showing intense CD with vari-ation of Ln^{III} and/or M^I ions will be useful to examine the chiroptical spectral−structure relation and important roles in configurational chirality for chemical sensors, NMR shift reagents, or chiral catalysis. Further, new coordination chemistry will be opened in combination of both lanthanide and alkaline metal ions or s−f dinuclear complexes with CF unity.

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