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Structure–chiroptical property relationship of kinetically labile camphor-derivative β -diketone Yb(III) complexes: do the adducts coexist as diastereomers or not?†

Yiji Lin,^a Shigang Wan,^a Fang Zou,^a Yuekui Wang^{*b} and Hui Zhang^{*a}

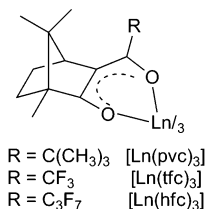
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The present work examines the relationship between the crystal structures and chiroptical properties of four chiral Yb(III) complexes with camphor-derivative β -diketone ligands by means of solid-state circular dichroism (CD) spectroscopy. For the seven-coordinate complexes, [Yb(H₂O)(*d*-hfc)₃] (**I**) and [Yb(H₂O)(*l*-hfc)₃] (**II**) (*d/l*-hfc[−] = 3-heptafluorobutyryl-(+)/(−)-camphorate), the *A*- and *A*-diastereomers coexist in their crystals and no apparent bisignate couplets are observed in their solid-state CD spectra. A theoretical study indicates that the ground-state energy difference between the two diastereomers **I** and **II** is only 0.913 kcal mol^{−1}, which explains why they could coexist in a crystal environment with the ratio of 1 : 1. While, eight-coordinate complexes *A*-[Yb(TPPO)₂(*d*-hfc)₃]·CHCl₃·3C₆H₁₂ (**III**) and *A*-[Yb(TPPO)₂(*l*-hfc)₃]·CHCl₃·3C₆H₁₂ (**IV**) (TPPO = triphenylphosphine oxide) are enantiopure in the solid-state, and typically negative and positive exciton splitting patterns around 330 nm are observed in their solid-state CD spectra. The solid-state CD spectra of these four complexes are in accordance with their X-ray single-crystal analyses. Besides, their solution CD spectra show that no particular isomer predominates in solution.

Introduction

The higher demand for labile chiral-at-metal complexes as chiral reagents is increasing quickly with the development of chirotechnology.¹ Lanthanide shift reagents containing chiral camphor-derivative β -diketonate ligands have received considerable attention² since Whitesides and Lewis first reported the application of [Eu(*d*-pvc)₃] (*d*-pvc[−] = 3-(*tert*-butylhydroxymethylene)-(+)-camphorate, Scheme 1) in direct determination of enantiomeric compositions of chiral substrates in 1970.³ More interestingly, [Ln(*d*-hfc)₃] (Ln = Pr, Eu, Er and Yb) were demonstrated to be effective receptors in enantioselective extraction of unprotected chiral amino acids.⁴ The chiral



Scheme 1 [Ln(cdkt)₃] (cdkt[−] = chiral camphor-derivative β -diketonate).

recognition between the substrates and shift reagents was realized *via* diastereomeric complexation in binding of the amino acids to form a seven-coordinate 1:1 receptor–amino acid adduct.^{4a} However, the detailed conformation or absolute configuration of these adducts remains to be elucidated for further understanding of the chiral discrimination.

Recent studies⁵ have revealed that reducing the symmetry of the adducts with a square anti-prism (SAP) geometry formed from the camphor-derivative β -diketone Eu(III) complexes and phosphine oxide ligands could effectively improve their luminescence properties because the metal-centered chirality is homologous with the *f*-*f* chromophores. Furthermore, it is reported that the complexes existed as enantiomers or concomitant diastereomers may exhibit different photochemical properties.⁶ In fact, most of the mononuclear lanthanide complexes could not retain their given metal-centered chirality due to their kinetic lability in solution. As a result, a mixture of

^a State Key Laboratory of Physical Chemistry of Solid Surface and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China. E-mail: hui Zhang@xmu.edu.cn; Fax: +86 592-2089057; Tel: +86 592-2183910

^b Key Laboratory of Chemical Biology and Molecular Engineering of the Education Ministry, Institute of Molecular Science, Shanxi University, Taiyuan 030006, China. E-mail: ykwang@sxu.edu.cn; Fax: +86 351-7017662; Tel: +86 351-7017662

† Electronic supplementary information (ESI) available: Fig. S1–S5, Fig. S7 (electronic absorption spectrum of **I**), Fig. S6 and S8 (electronic absorption spectrum of **III**), Fig. S9 (ORTEP structures of **I** and **II**), and Fig. S10 (ORTEP structures of **III** and **IV**). CCDC reference numbers 772227 (**I**), 764761 (**II**), 777709 (**III**) and 777708 (**IV**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1nj20430k

diastereomers associated with quick quasi-racemization may form in solution,⁶ and sometimes coexists in the single crystals of the adducts of tris(β -diketonato) Ln(III) complexes with other ligands.^{5,6b,7} Additionally, almost all the studies of above-mentioned chiral adducts were interested in the solution chiroptical properties of the chelates. However, the solution and solid-state stereostructures of these chiral labile complexes are different. It is difficult to predict their solution or solid-state structures only by single crystal structures or solution CD spectra, respectively. Therefore, combining solid-state chiroptical spectra and XRD patterns of bulk products with the single-crystal analysis is very important to examine the conformations of chiral labile lanthanide complexes in the solid state.^{6a,8} Besides, the comparison of the solution and the solid-state structure of these complexes may be favorable for us to investigate the reaction mechanisms of the configurational chirality transformation. Unfortunately, only a few reported structures of chiral camphor-derivative β -diketon lanthanide complexes and their adducts formed by chelating with substrates are available for such comparison.^{5,9}

Previous studies have demonstrated that some adducts may exist as the enantiopure solid phases⁵ but in most cases they preferred to form kinds of diastereomers owing to their kinetic lability in solution.^{2c,10} As far as we know, the metal-centered chiralities of enantiopure β -diketon metal complexes with three or four helically bladed propellers could be characterized by the CD couplet patterns in the strong π - π^* transition region of ligands.^{11,6a,9a} However, Kawai *et al.* have reported that no bisignate couplet in the solution CD spectrum of [Eu(TPPO)₂(*d*-tfc)₃] was observed even though this adduct is enantiopure in the solid state.⁵ Herein, we suppose that there must be typical exciton splitting patterns in the solid-state CD spectra for such enantiopure adducts.^{6a,11}

To verify this supposition, we decided to investigate the structures and solid-state CD spectra of both concomitant diastereomeric and enantiopure adducts of the camphor-derivative β -diketon lanthanide complexes. Fortunately, a pair of diastereomer coexisting complexes, [Yb(H₂O)(*d*-hfc)₃] (**I**) and [Yb(H₂O)(*l*-hfc)₃] (**II**), and the other pair of enantiopure complexes, [Yb(TPPO)₂(*d*-hfc)₃]·CHCl₃·3C₆H₁₂ (**III**) and [Yb(TPPO)₂(*l*-hfc)₃]·CHCl₃·3C₆H₁₂ (**IV**), were obtained. Based on the solid-state CD spectra and XRD patterns of bulk products with the single-crystal analysis, the relationship between the crystal structures and chiroptical properties of the four complexes is established. In addition, the solution CD spectra of the four complexes were also measured to investigate their conformations in solution.

Experimental

Solution and solid state CD spectra were recorded with a JASCO J-810 spectropolarimeter. Powder XRD patterns were obtained in a Panalytical X-pert diffractometer with Cu K α radiation. Electronic absorption spectra were obtained on a Varian-Cary 5000 spectrophotometer. For the solid-state CD and electronic absorption spectra, crystalline samples were ground to fine powders with potassium chloride and compressed into transparent disks. The concentration of the disks was 1.00 mg per 300 mg (sample/KCl) for CD spectra

measurement. The solution CD and electronic absorption spectra were measured in hexane. The concentration of the solution was 2×10^{-5} mol L⁻¹. Elemental analyses for C and H were performed on an Elementar Vario EL III elemental analyzer.

All solvents were of reagent grade and were used as received. *d*-Hhfc and *l*-Hhfc were purchased from Alfa Aesar and Aldrich, respectively.

X-Ray data were collected on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at 298 K. Empirical absorption corrections were applied to the data using the multiscan program SADABS.¹² The structures were solved by the direct method using SHELXS-97 program and refined by the full-matrix least-square method on F^2 with the SHELXL-97 program.^{13,14} The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and not refined. All calculations were carried out using the SHELXTL crystallographic software package.¹⁵ All crystallographic data are given in Tables 1 and 2. For complexes **III** and **IV**, the lattices contain large solvent accessible voids, but the solvent was highly disordered and therefore could not be modeled. Instead, the disordered solvent was accounted for using the program SQUEEZE,¹⁶ which estimated that 216 electrons were located in the voids of 1182.5 Å³ for **III** and 188 electrons were located in the voids of 1201.8 Å³ for **IV**. These results indicate that each unit cell of **III** or **IV** contains 1 molecule of CHCl₃ and 3 molecules of hexane, and these solvent molecules were included in the formula in Table 2. CCDC 772227 (**I**), 764761 (**II**), 777709 (**III**), and 777708 (**IV**) contain the supplementary crystallographic data (excluding structure factors) for this paper (ESI†).

[Yb(H₂O)(*d*-hfc)₃] (**I**)

d-Hhfc (0.1671 g, 0.48 mmol) was stirred with Et₃N (0.0485 g, 0.48 mmol) in CHCl₃ (15 mL) at room temperature for 10 min. Then, an aqueous solution (7.5 mL) of YbCl₃·6H₂O (0.0609 g, 0.16 mmol) was added. After stirring for another 30 min,

Table 1 Crystallographic data for **I** and **II**

Compound reference	I	II
Chemical formula	C ₄₂ H ₄₄ F ₂₁ O ₇ Yb	C ₄₂ H ₄₄ F ₂₁ O ₇ Yb
Formula mass	1232.81	1232.81
Crystal system	Monoclinic	Monoclinic
<i>a</i> /Å	24.573(6)	24.575(5)
<i>b</i> /Å	13.207(3)	13.191(3)
<i>c</i> /Å	31.227(8)	31.096(6)
α /°	90.00	90.00
β /°	92.072(5)	91.925(4)
γ /°	90.00	90.00
Unit cell volume/Å ³	10 127(4)	10 075(3)
Temperature/K	298(2)	298(2)
Space group	C2	C2
<i>Z</i>	8	8
Absorption coefficient, μ /mm ⁻¹	1.969	1.979
<i>F</i> (000)	4888	4888
No. of reflections measured	27 414	27 046
No. of independent reflections	17 888	18 440
<i>R</i> _{int}	0.0716	0.0275
Final <i>R</i> ₁ values (<i>I</i> > 2 σ (<i>I</i>))	0.0716	0.0481
Final <i>wR</i> (<i>F</i> ²) values (<i>I</i> > 2 σ (<i>I</i>))	0.1472	0.1055
Final <i>R</i> ₁ values (all data)	0.1183	0.0636
Final <i>wR</i> (<i>F</i> ²) values (all data)	0.1616	0.1110
Goodness of fit on <i>F</i> ²	0.904	0.977
Flack parameter	0.044(12)	0.009(9)

Table 2 Crystallographic data for **III** and **IV**

Compound reference	III	IV
Chemical formula	C _{84.33} H _{78.33} ⁻ ClF ₂₁ O ₈ P ₂ Yb	C _{84.33} H _{78.33} ⁻ ClF ₂₁ O ₈ P ₂ Yb
Formula mass	1889.23	1889.23
Crystal system	Trigonal	Trigonal
<i>a</i> /Å	14.800(3)	14.862(2)
<i>b</i> /Å	14.800(3)	14.862(2)
<i>c</i> /Å	34.447(11)	34.432(8)
α /°	90.00	90.00
β /°	90.00	90.00
γ /°	120.00	120.00
Unit cell volume/Å ³	6535(3)	6586(2)
Temperature/K	298(2)	298(2)
Space group	<i>P</i> 3(2)	<i>P</i> 3(1)
<i>Z</i>	3	3
Absorption coefficient, μ /mm ⁻¹	1.238	1.228
<i>F</i> (000)	2863	2863
No. of reflections measured	34 806	50 295
No. of independent reflections	13 049	17 175
<i>R</i> _{int}	0.0268	0.0311
Final <i>R</i> ₁ values (<i>I</i> > 2 σ (<i>I</i>))	0.0622	0.0653
Final <i>wR</i> (<i>F</i> ²) values (<i>I</i> > 2 σ (<i>I</i>))	0.1677	0.1761
Final <i>R</i> ₁ values (all data)	0.0713	0.0776
Final <i>wR</i> (<i>F</i> ²) values (all data)	0.1759	0.1860
Goodness of fit on <i>F</i> ²	1.164	1.009
Flack parameter	0.052(10)	0.042(10)

the chloroform layer was separated. An excess amount of Na₂SO₄ was added to dry the organic phase overnight. Then the solution was concentrated to a yellow oil and 20 mL of acetonitrile was added and allowed to stand at room temperature for a slow evaporation over several days, pale yellow crystals were obtained. Yield 47.4%. Anal. calcd for [Yb(*d*-hfc)₃(H₂O)]: C, 40.91; H, 3.59%. Found: C, 40.95; H, 3.56%.

[Yb(H₂O)(*l*-hfc)₃] (**II**)

Complex **II** was prepared following a similar procedure as described for **I** just by replacing *d*-Hhfc with *l*-Hhfc in 64.4% yield. Anal. calcd for [Yb(*l*-hfc)₃(H₂O)]: C, 40.91; H, 3.59%. Found: C, 40.87; H, 3.62%.

[Yb(TPPO)₂(*d*-hfc)₃]·CHCl₃·3C₆H₁₂ (**III**)

Complex **I** (0.02 mmol) and TPPO (0.04 mmol) were dissolved in CH₃OH (10 mL) and refluxed under stirring overnight. The reaction solution was evaporated under reduced pressure, which gave a white powder. Recrystallization with CHCl₃/*n*-hexane solution gave colorless block crystals. Yield 90.5%. Anal. calcd for [Yb(TPPO)₂(*d*-hfc)₃]: C, 52.88; H, 4.09%. Found: C, 52.48; H, 3.95%.¹⁷

[Yb(TPPO)₂(*l*-hfc)₃]·CHCl₃·3C₆H₁₂ (**IV**)

Complex **IV** was prepared following a similar procedure as described for **III** just by replacing complex **I** with complex **II** in 88.3% yield. Anal. calcd for [Yb(TPPO)₂(*l*-hfc)₃]: C, 52.88; H, 4.09%. Found: C, 52.88; H, 4.32%.¹⁷

Results and discussion

Crystal structures

[Yb(H₂O)(*d*-hfc)₃] (**I**) and [Yb(H₂O)(*l*-hfc)₃] (**II**). The crystal structure analysis of complex **I** shows that the asymmetric unit

within the unit cell consists of two independent molecules **Ia** and **Ib** (Fig. 1). Each Yb(III) is bonded to seven oxygen atoms from three chiral bidentate diketone anions and a water molecule, respectively, to form a distorted capped trigonal prism. The left-handed helical arrangement of the three β -diketone ligands around the Yb1 denotes that the absolute configuration of **Ia** is Δ .¹¹ In contrast, the metal-centered chirality of **Ib** is Λ . It is worthy of note that the molecules **Ia** and **Ib** with the same chiral ligand *d*-hfc⁻ are not the enantiomers of each other, while their coordination polyhedra may be considered as mutual pseudo-enantiomers due to their approximately symmetrical “mirror image” relation (Fig. S1, ESI[†]).

Selected bond lengths and angles of complex **I** are summarized in Table 3. Yb–O bond lengths are between 2.20–2.33 Å and 2.18–2.35 Å in the Yb1 and Yb2 moieties, which are very similar to those found in [Yb(H₂O)(acac)₃] (Hacac = acetylacetonate).¹⁸ It is also worth mentioning that two independent molecules exist in the crystal of [Yb(H₂O)(acac)₃] as a pair of enantiomers because they are symmetric as mirror images.

Complex **II** was prepared by using *l*-hfc⁻ instead of the *d*-form. As in the previous case, diastereomeric Δ -[Yb(H₂O)(*l*-hfc)₃] (**IIa**) and Λ -[Yb(H₂O)(*l*-hfc)₃] (**IIb**) coexist in the crystal, and the coordination polyhedra of **IIa** and **IIb** are also considered to be approximately symmetric as “mirror images” (Fig. S1, ESI[†]). Selected bond lengths and angles are summarized in Table 3. Apparently, **Ia** and **IIa**, **Ib** and **IIb** are two pairs of enantiomers, which have been demonstrated by their crystal structure analyses.

In molecule **Ia**, the least-squares plane of the β -diketone group containing O1O2 is denoted as α 1. Similarly, the least-squares planes of the other two β -diketone groups are denoted as β 1 and γ 1 (Fig. 1). The angle between the O1W–Yb1 bond and α 1, β 1, and γ 1 planes is 74.5(4)°, 48.5(3)°, and 9.0(3)°, respectively. The plane γ 1 is nearly parallel to the O1W–Yb1 bond. The dihedral angle between α 1 and β 1, β 1 and γ 1, and α 1 and γ 1 is 63.4(4)°, 74.0(5)°, and 89.3(4)°, respectively. The plane α 1 is perpendicular to the plane γ 1.

For molecule **Ib**, the least-squares planes of the three β -diketone groups are denoted as α 2, β 2, and γ 2 as shown in Fig. 1. The angle between the O2W–Yb2 bond and α 2, β 2, and γ 2 planes is 79.1(4)°, 44.6(3)°, and 10.8(3)°, respectively. The dihedral angle between α 2 and β 2, β 2 and γ 2, and α 2 and γ 2 is 55.4(5)°, 64.6(5)°, and 85.4(4)°, respectively. It means that the coordination environment around the Yb(III) in **Ib** is different from that of **Ia**. Neither are the structure parameters of **IIa** the same as those of **IIb** in complex **II**. Accordingly, the chiroptical signals originated from the Λ - and Δ -configurational chiralities of the two diastereomers in complex **I** or **II** may be diverse in magnitude and located at a slightly different wavelength in the same region. For all that, the solid-state chiroptical spectra of complex **I** or **II** could be expected as a sum of the chiroptical signals from both diastereomers.

Besides, the observed and simulated XRD patterns of complex **I** were found to be almost identical (Fig. S2, ESI[†]), which indicates that its bulk sample is a pure phase.

To get an insight into the coexistence of the two absolute configurations of **I** in crystal, the geometries of diastereomers **Ia** and **Ib** in methanol solution have been optimized using the

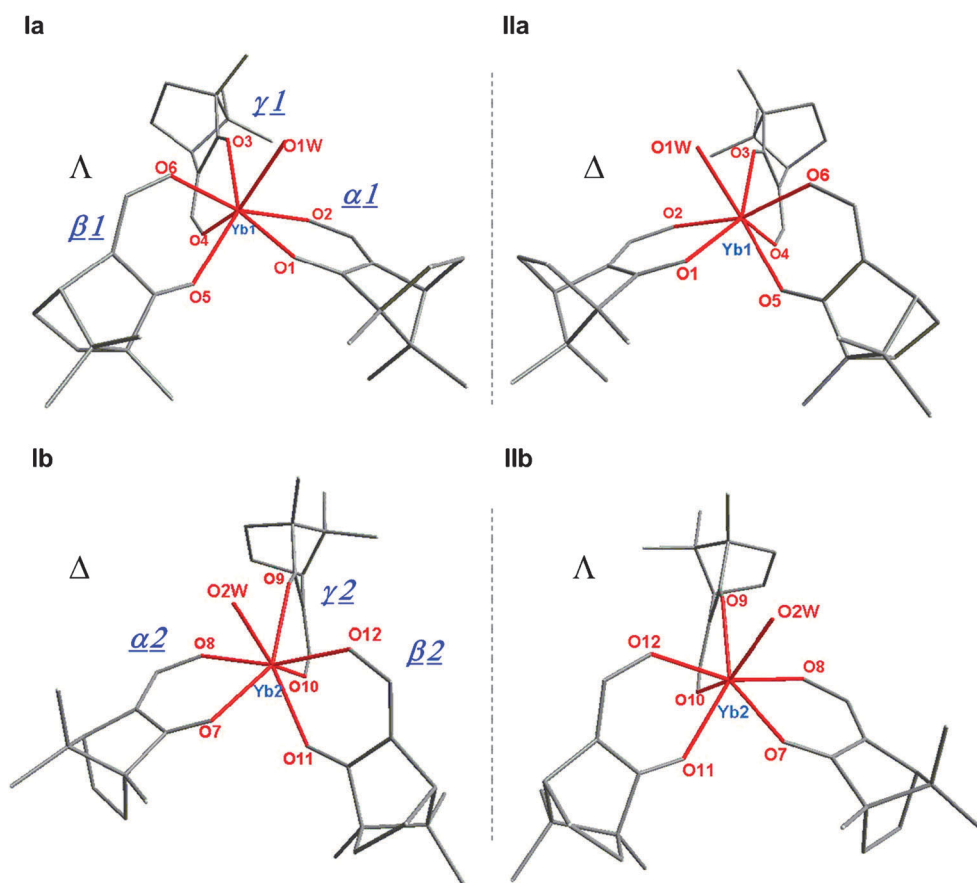


Fig. 1 Independent molecules **Ia**, **Ib** of complex **I** and **IIa**, **IIb** of complex **II** ($-\text{C}_3\text{F}_7$ groups are omitted for clarity).

Table 3 Selected bond lengths (Å) and angles (°) for **I** and **II**

	Molecule a		Molecule b	
I	Yb1–O1	2.271(8)	Yb2–O7	2.254(7)
	Yb1–O2	2.182(8)	Yb2–O8	2.200(9)
	Yb1–O3	2.330(9)	Yb2–O9	2.320(8)
	Yb1–O4	2.204(8)	Yb2–O10	2.180(9)
	Yb1–O5	2.264(9)	Yb2–O11	2.243(9)
	Yb1–O6	2.239(8)	Yb2–O12	2.246(8)
	Yb1–O1W	2.329(8)	Yb2–O2W	2.359(8)
	O1–Yb1–O2	76.6(4)	O7–Yb2–O8	74.9(4)
	O3–Yb1–O4	74.9(4)	O9–Yb2–O10	74.9(3)
	O5–Yb1–O6	76.8(4)	O11–Yb2–O12	77.3(3)
II	Yb1–O1	2.281(4)	Yb2–O7	2.258(5)
	Yb1–O2	2.201(5)	Yb2–O8	2.205(5)
	Yb1–O3	2.321(5)	Yb2–O9	2.305(5)
	Yb1–O4	2.202(5)	Yb2–O10	2.181(5)
	Yb1–O5	2.253(6)	Yb2–O11	2.258(5)
	Yb1–O6	2.223(5)	Yb2–O12	2.243(4)
	Yb1–O1W	2.325(5)	Yb2–O2W	2.335(5)
	O1–Yb1–O2	77.6(2)	O7–Yb2–O8	76.4(2)
	O3–Yb1–O4	75.5(2)	O9–Yb2–O10	76.1(2)
	O5–Yb1–O6	77.0(2)	O11–Yb2–O12	76.86(19)

Gaussian03 program package¹⁹ at the DFT/B3LYP level with the default PCM solvent model and the mixed basis set: SBKJC²⁰ for the central metal ion, and 6-31G* for other atoms. The results show that the ground-state energy of **Ia** is only 0.913 kcal mol⁻¹ higher than that of **Ib**. In other words, the probabilities of the two diastereomers in solution are nearly identical with a deviation of less than 0.15% under

room temperature. Therefore, they could coexist in a crystal environment with the ratio of 1 : 1.

[Yb(TPPO)₂(*d*-hfc)₃]·CHCl₃·3C₆H₁₂ (III) and [Yb(TPPO)₂(*t*-hfc)₃]·CHCl₃·3C₆H₁₂ (IV). The crystal structure analysis shows that the complexes **III** and **IV** (Fig. 2) are analogous to [Eu(TPPO)₂(*d*-tfc)₃]⁵ (*d*-tfc⁻ = 3-trifluoroacetyl-(+)-camphorate, Scheme 1). Since they are a pair of enantiomers, only the crystal structure of **III** is described here. As indicated in Fig. 2A, six O atoms from three chiral diketone anions and two O atoms from two TPPO ligands coordinate to a Yb(III) cation to form a square anti-prism (SAP, Fig. 2B). Selected bond lengths and angles of the two complexes are summarized in Table 4. Yb–O bond lengths are between 2.27–2.42 Å and 2.28–2.43 Å in **III** and **IV**, respectively, which are close to those found in [Yb(*S*-BINAPO)(hfa)₃]^{6b} (*S*-BINAPO = 1,1'-binaphthyl phosphine oxide; hfa⁻ = hexafluoroacetyl-acetate). In the SAP geometry around the Yb(III) cation, O1O2O3O22 and O4O6O5O11 are taken as the top and bottom planes of the anti-prism, respectively, and their dihedral angle is 2.1°. The mean deviations of the two planes are 0.1608 and 0.1555 Å, respectively. Additionally, the top plane is rotated *anti*-clockwise by 42.5° relative to the bottom plane, which is near the theoretical value of 45° for a regular SAP geometry suggested by Parker and Williams²¹ and indicates that the absolute configuration around the Yb(III) cation is Δ .²² Similarly, the configurational chirality around the Yb(III) cations in **IV** could be assigned as Λ . In addition, the X-ray diffraction

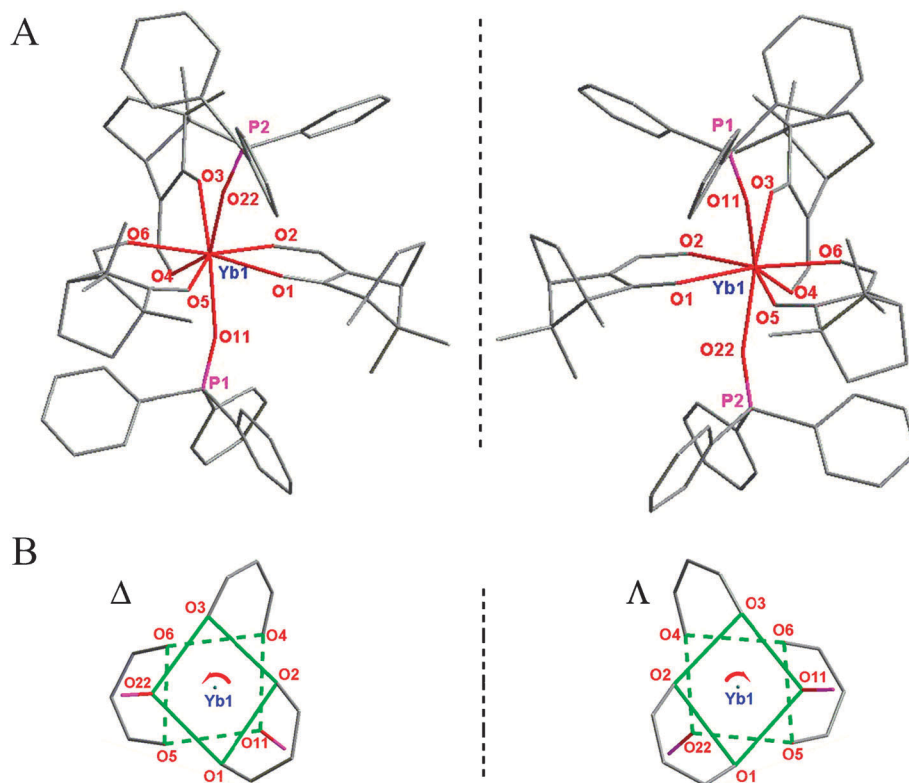


Fig. 2 (A) Molecular structures of **III** (left) and **IV** (right) ($-C_3F_7$ groups are omitted for clarity). (B) The coordination polyhedrons and absolute configurations of **III** (left) and **IV** (right).

Table 4 Selected bond lengths (Å) and angles (°) for **III** and **IV**

	III		IV	
Distance	Yb1–O1	2.419(7)	Yb1–O1	2.418(6)
	Yb1–O2	2.290(7)	Yb1–O2	2.311(7)
	Yb1–O3	2.331(6)	Yb1–O3	2.330(5)
	Yb1–O4	2.338(6)	Yb1–O4	2.352(5)
	Yb1–O5	2.404(6)	Yb1–O5	2.433(6)
	Yb1–O6	2.278(6)	Yb1–O6	2.295(6)
	Yb1–O11(P1)	2.279(5)	Yb1–O11(P1)	2.293(5)
	Yb1–O22(P2)	2.291(5)	Yb1–O22(P2)	2.287(5)
Angles	O1–Yb1–O2	73.5(2)	O1–Yb1–O2	73.8(2)
	O3–Yb1–O4	74.7(2)	O3–Yb1–O4	74.18(19)
	O5–Yb1–O6	72.4(2)	O5–Yb1–O6	72.0(2)
	O11–Yb1–O22	142.79(18)	O11–Yb1–O22	142.89(17)

analysis of **III** (Fig. S3, ESI†) indicates the formation of a pure phase.

The S angle^{5,23} (eqn (1)), the minimal variance of dihedral angles along all edges, was introduced to evaluate the degree of the distortion of the coordination polyhedron of the Yb(III) center of **III** and **IV** from an ideal SAP geometry based on the “shape measure” criterion.

$$S(\delta, \theta) = \min \sqrt{\left[\left(\frac{1}{m} \right) \sum_{i=1}^m (\delta_i - \theta_i)^2 \right]} \quad (1)$$

where m , δ_i , θ_i are the number of all possible edges (here $m = 18$), the observed dihedral angle between planes along the i th edge of the experimental polyhedron, and the dihedral angle of the corresponding ideal polyhedron, respectively. The S values of

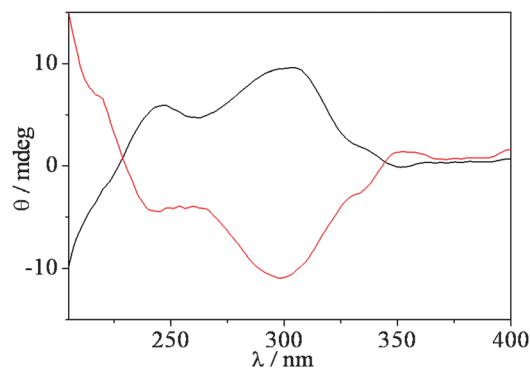


Fig. 3 Solid-state CD spectra of crystals **I** and **II** (black: **I**; red: **II**).

III and **IV** are 8.0° and 8.2° , respectively. They are close to the S angle of $[\text{Eu}(\text{TPPO})_2(d\text{-tfc})_3]^5$ (6.36°) which has a SAP coordination geometry around the Eu(III) cation.

CD spectra

As we predicted, no apparent bisignate couplets were observed in the solid-state CD spectra (Fig. 3) of crystals **I** and **II**. It proved that a mixture of diastereomers coexists in the solid state because an enantiopure β -diketone metal complex could exhibit a characteristic pattern of the exciton band in the strong π - π^* transition region.^{11,6a,9a,b} Besides, the same shapes of the solid-state CD curves were obtained using the bulk samples (Fig. S4, ESI†) as well. The solid-state CD spectra of **III** and **IV** are shown in Fig. 4. Here, the typically negative and

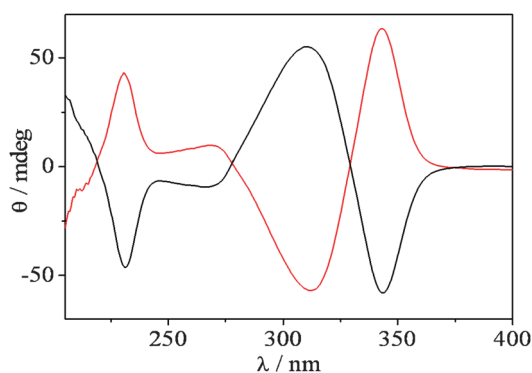


Fig. 4 Solid-state CD spectra of **III** and **IV** (black: **III**; red: **IV**).

positive CD couplets around 330 nm are arising from the π - π^* transition of the β -diketone ligands, which indicates that the SAP configurations of the two complexes are Δ and Λ , respectively.^{11,6a,9a,b} These results are in accordance with the crystal structure analysis. In addition, the strong negative and positive Cotton effects centered around 230 nm in the solid-state CD spectra of **III** and **IV** are assigned to the π - π^* transition of the TPPO ligands.

Besides, the absence of the bisignate couplets in the solution CD spectra of the four complexes (Fig. 5 and 6) indicates that no particular isomer predominates in solution and quasi-racemization may occur during the dissolution of **III** and **IV** due to their kinetic lability. The Cotton effects observed in the CD spectra are mainly induced by the asymmetric carbon atoms on the ligand.

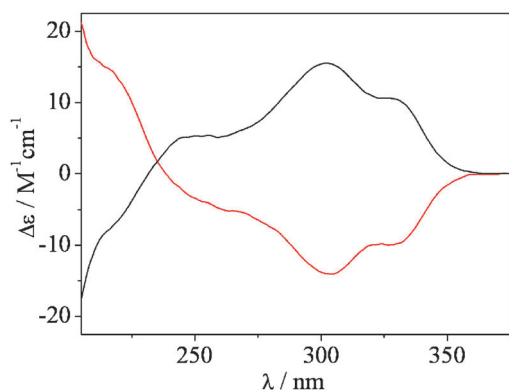


Fig. 5 Solution CD spectra of **I** and **II** (black: **I**; red: **II**).

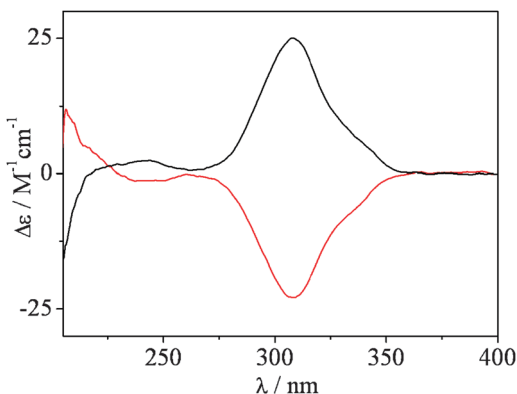


Fig. 6 Solution CD spectra of **III** and **IV** (black: **III**; red: **IV**).

Conclusions

The structures and solid-state CD spectra of two pairs of adducts of chiral camphor-derivative β -diketone Yb(III) complexes with H₂O or TPPO ligands, [Yb(H₂O)(*d*-hfc)₃] (**I**), [Yb(H₂O)(*l*-hfc)₃] (**II**), Δ -[Yb(TPPO)₂(*d*-hfc)₃]·CHCl₃·3C₆H₁₂ (**III**) and Λ -[Yb(TPPO)₂(*l*-hfc)₃]·CHCl₃·3C₆H₁₂ (**IV**), have been studied for the first time. As we expected, the solid-state CD spectra combined with the observed and simulated XRD patterns of the bulk products of **I** and **II** indicated that two diastereomers with opposite metal-centered chirality coexisted in each single crystal. The DFT calculations show that there is only a 0.913 kcal mol⁻¹ energy difference between the two diastereomers of **I**, which could explain why they coexisted in a crystal environment with the ratio of 1:1. In contrast, complexes **III** and **IV** are enantiopure in the solid-state, which was further confirmed by the typical negative and positive exciton splitting patterns in their solid-state CD spectra as well as the single-crystal structure and XRD characterization, respectively. Accordingly, it is now possible to examine whether these four adducts coexisted as diastereomers or not in their solid-state by the relationship between the crystal structures and the solid-state chiroptical properties. Furthermore, owing to the kinetic lability of the lanthanide ions, no particular isomer of the four complexes predominates in solution, which has been demonstrated by their solution CD spectra.

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