

Supporting Information

Identification of Geometrical Isomers Using Vibrational Circular Dichroism Spectroscopy: A Series of Mixed-Ligand Complexes of Diamagnetic Co(III) Ions

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Chromatographic separation of the bis(tfac) complexes of $[\text{Co}(\text{tfac})_2(\text{acac})]$

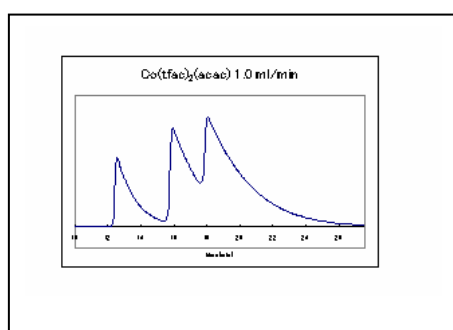


Figure S1. Chromatographic separation of the bis(tfac) complexes of $[\text{Co}(\text{tfac})_2(\text{acac})]$ The complexes were eluted with benzene at a flow rate of 1 mLmin^{-1} by silica gel column. The first, second and third peak is identified as **trans-cis**, **cis-trans** and **cis-cis** isomers, respectively.

¹H NMR

The ¹H NMR spectra (JNM-AL400, JEOL, Japan) were measured on the CDCl₃ solutions of metal complexes. The chemical shift values (δ) and peak areas are given below.

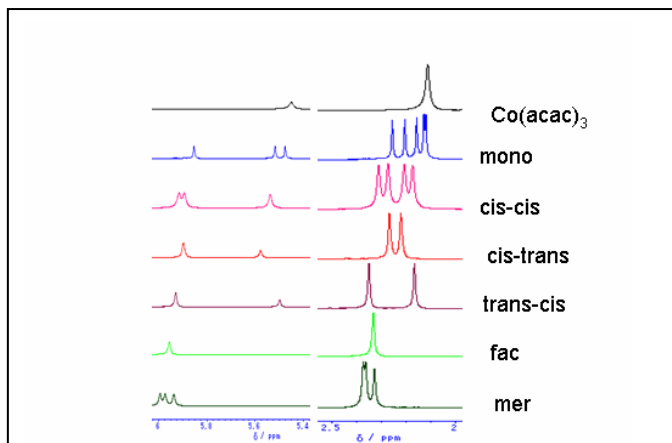


Figure S2. The ¹H NMR spectra were measured on the CDCl₃ solutions of metal complexes:

[Co(tfac)_n(acac)_{3-n}] (n = 0 ~ 3): (a) mono(tfac) complexes (n = 1); (b) bis(tfac) complexes (n = 2); (**trans-cis**, **cis-trans** and **cis-cis**) (c) tris(tfac) complexes (n = 3) (**mer** and **fac**).

Co(tfac)(acac)₂: (400 MHz, CDCl₃) δ(ppm) 5.85 (s,1H), 5.52 (s,1H), 5.48 (s,1H), 2.26 (s,3H), 2.20 (s,3H), 2.16 (s,3H), 2.13 (s,3H), 2.12 (s,3H)

trans-cis – [Co(tfac)₂(acac)]: (400 MHz, CDCl₃) δ (ppm) 5.93 (s,2H), 5.50 (s,1H), 2.35 (s,6H), 2.16 (s,6H)

cis-trans – [Co(tfac)₂(acac)]: (400 MHz, CDCl₃) δ (ppm) 5.90 (s,2H), 5.58 (s,1H), 2.27 (s,6H), 2.22 (s,6H)

cis-cis – [Co(tfac)₂(acac)]: (400 MHz, CDCl₃) δ (ppm) 5.92 (s,1H), 5.90 (s,1H), 5.54 (s,1H), 2.31 (s,3H), 2.27 (s,3H), 2.21 (s,3H), 2.17 (s,3H)

fac – [Co(tfac)₃]: (400 MHz, CDCl₃) δ (ppm) 5.96 (s,3H), 2.33 (s,3H)

mer – [Co(tfac)₃]: (400 MHz, CDCl₃) δ (ppm) 5.99 (s,1H), 5.97 (s,1H), 5.94 (s,1H), 2.37 (s,3H), 2.36 (s,3H), 2.33 (s,3H)

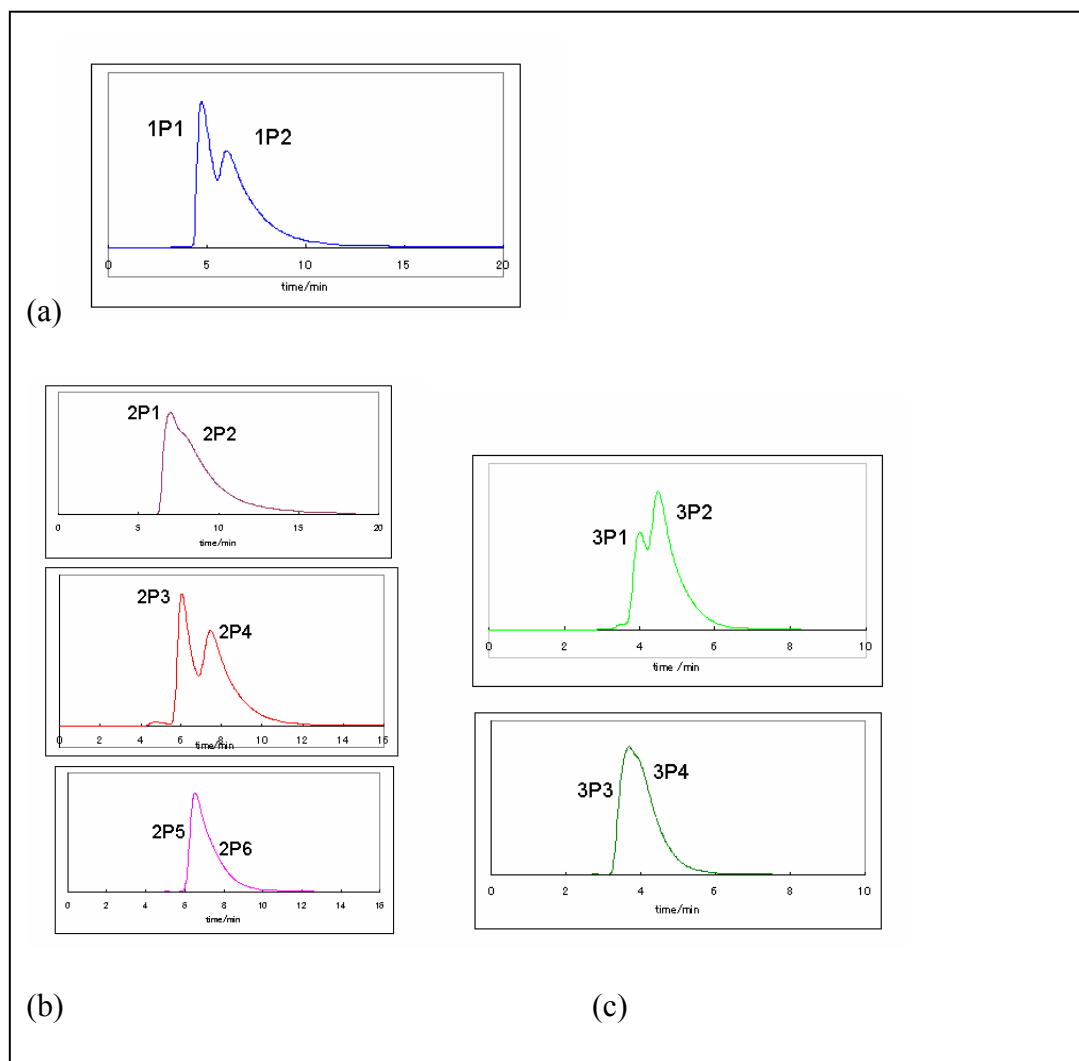


Figure S3. Chromatograms for the separation of the enantiomer pairs of $[\text{Co}(\text{tfac})_n(\text{acac})_{3-n}]$ ($n = 0 \sim 3$): (a) mono(tfac) complex ($n = 1$); (b) bis(tfac) complexes ($n = 2$); (c) tris(tfac) complexes ($n = 3$). The complexes were eluted with methanol at a flow rate of $1 \text{ mL}\cdot\text{min}^{-1}$ and 40°C . The column was packed with an ion-exchange adduct of $\Delta\text{-}[\text{Ru}(\text{phen})_3]^{2+}$ /synthetic hectorite.

Two peaks (denoted by 1P_1 and 1P_2 , respectively) were obtained in $[\text{Co}(\text{tfac})(\text{acac})_2]$.

A racemic mixture of bis(tfac) complexes **trans-cis**, **cis-trans** and **cis-cis**- $[\text{Co}(\text{tfac})_2(\text{acac})]$ was eluted with methanol on the same column after silica gel column of HPLC. These peaks (denoted by **trans-cis** (2P_1 , 2P_2), **cis-trans** (2P_3 , 2P_4) and **cis-cis** (2P_5 , 2P_6), respectively) were obtained.

The fac- $[\text{Co}(\text{tfac})_3]$ was eluted with methanol on the same column. The peaks (denoted by 3P_1 , 3P_2 , respectively) were obtained on separation. The mer- $[\text{Co}(\text{tfac})_3]$ is not separated by two parts. We have two sections of collected and named as 3P_3 and 3P_4 .

Circular dichroism spectra

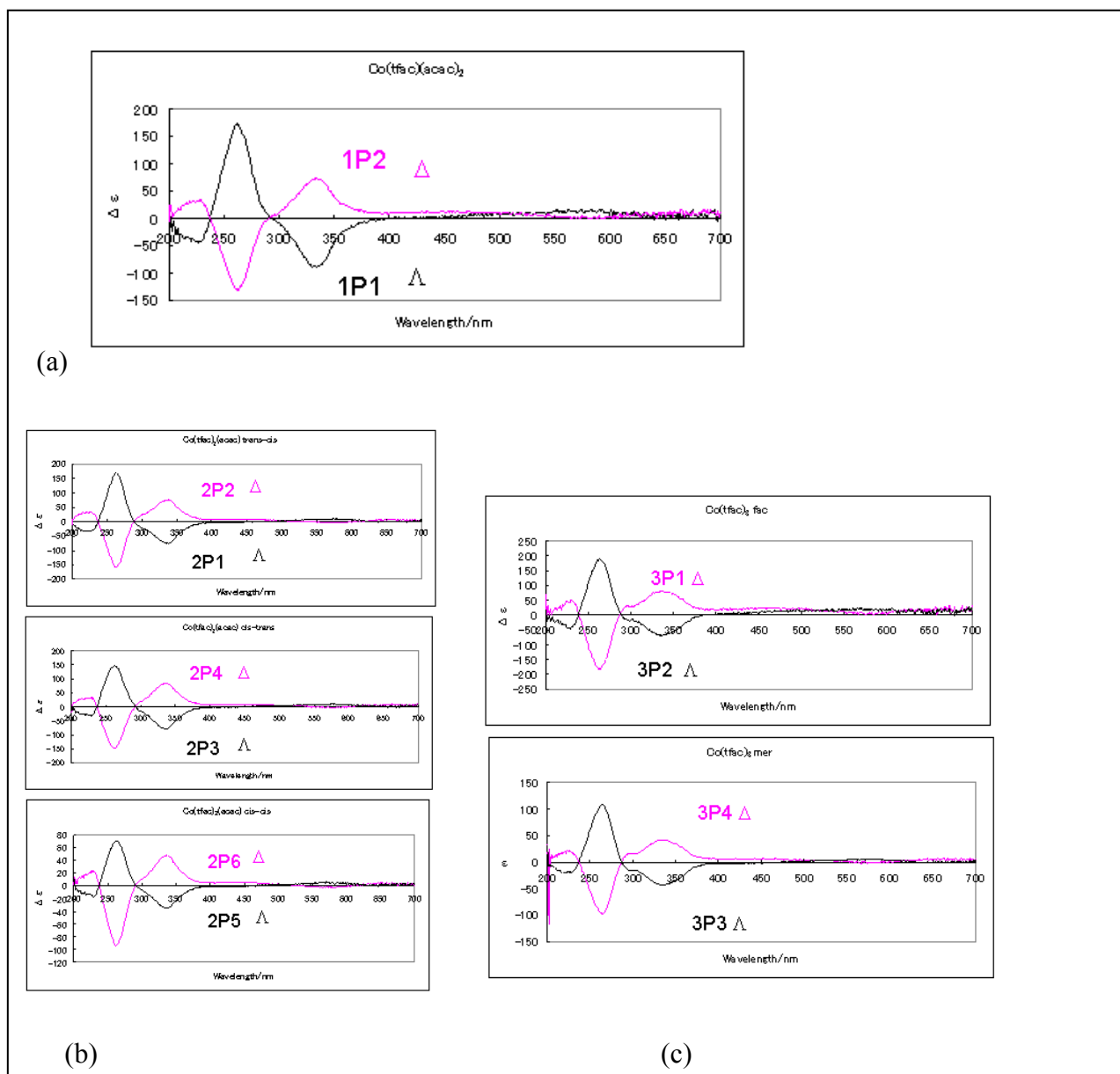


Figure S4. Circular dichroism spectra of $[\text{Co}(\text{tfac})_n(\text{acac})_{3-n}]$ ($n = 0 - 3$)

Black and pink curves are for Λ and Δ - isomer, respectively. From the CD spectra of these fractions, **3P₁** and **3P₂** of HPLC (Figure S3) were concluded to contain Δ -isomer and Λ -isomers, respectively. In other isomers, peak 1 and peak 2 were concluded to contain Λ - and Δ - isomer, respectively.

The molar extinction coefficient (ϵ) and $\Delta\epsilon$ were determined from the methanol solution of each isomer as given below.

[Co(tfac)(acac)₂]: ϵ (112.8 at 594 nm), ϵ (7115 at 325 nm) : (Λ -isomer): $\Delta\epsilon$ (-2.34 at 652 nm). $\Delta\epsilon$ (7.09 at 576 nm) (Δ -isomer): $\Delta\epsilon$ (+2.41 at 650 nm). $\Delta\epsilon$ (-4.93 at 571 nm), IR; ϵ 1852 (1521 cm^{-1})

[Co(tfac)₂(acac)]: trans-cis: ϵ (115.4 at 594 nm) , ϵ (6154 at 325 nm): Λ -isomer $\Delta\epsilon$ (-3.27 at 659 nm); $\Delta\epsilon$ (7.48 at 575 nm) Δ -isomer $\Delta\epsilon$ (+3.56 at 661 nm) $\Delta\epsilon$ (-6.43 at 572 nm) IR; ϵ 1015 (1522 cm^{-1})

cis-trans: ϵ (126 at 598 nm), ϵ (6194 at 325 nm) : (Λ -isomer): $\Delta\epsilon$ (-2.66 at 646nm); $\Delta\epsilon$ (6.72 at 574 nm) (Δ -isomer): $\Delta\epsilon$ (+3.16, 642nm); $\Delta\epsilon$ (-6.47 at 575 nm), IR IR; ϵ 902 (1522 cm^{-1})

cis-cis: ϵ (112 at 593 nm), ϵ (5872 at 325nm): (Λ -isomer): $\Delta\epsilon$ (-1.53at 647nm); $\Delta\epsilon$ (4.53 at 573 nm) (Δ -isomer): $\Delta\epsilon$ (+2.52, 651 nm); $\Delta\epsilon$ (-4.63at 576 nm), IR; ϵ 1090 (1521 cm^{-1})

[Co(tfac)₃]: fac: ϵ (112 at 596 nm) , ϵ (6194 at 325nm): (Λ -isomer): $\Delta\epsilon$ (-2.07at 653 nm); $\Delta\epsilon$ (7.21 at 577 nm) (Δ -isomer): $\Delta\epsilon$ (3.24 at 656 nm); $\Delta\epsilon$ (-6.86 at 578 nm), IR; ϵ 673 (1527 cm^{-1})

mer: ϵ (137 at 598 nm), ϵ (6487 at 325nm): (Λ -isomer): $\Delta\epsilon$ (-2.95 at 657 nm); $\Delta\epsilon$ (6.52 at 578 nm) (Δ -isomer): $\Delta\epsilon$ (3.57at 656 nm); $\Delta\epsilon$ (-4.54 at 577 nm), IR; ϵ 619 (1527 cm^{-1})

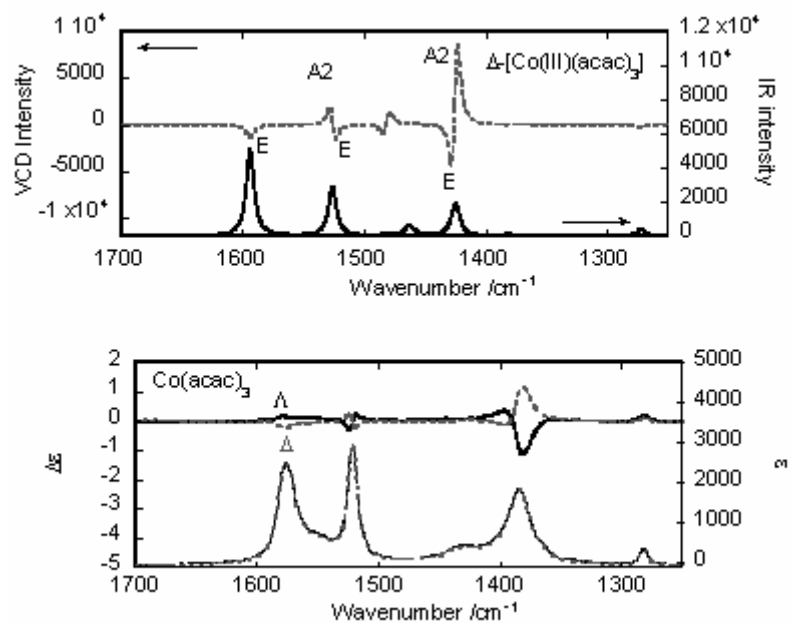


Figure S5. Vibrational circular dichroism spectra of Δ -Co(acac)₃: calculation (upper) and observation (lower) (solvent: CDCl₃).