(copolymer), 111291-35-1; 4-nitro-1,2-phenylenediamine, 99-56-9; salicylaldehyde, 90-02-8; terephthaloyl chloride, 100-20-9.

Supplementary Material Available: Tables of deviations (in angstroms) from the least-squares mean trapezoidal planes of the $Zr(adsp)_2$ coordination sphere and dihedral angles (Table V), torsion angles in the $adsp^{2-}$ ligands (Table VII), bond distances, bond angles, anisotropic temperature coefficients, and hydrogen atom coordinates (8 pages); a listing of observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

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Resolution and Circular Dichroism of the Optical Isomers of Tris(2,4-pentanedionato)ruthenium(III)

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The enantiomeric isomers of $[Ru^{III}(acac)_3]$ (acac = 2,4-pentanedionate) were completely resolved by HPLC on a column of porous silica gel coated with cellulose tris(phenylcarbamate). The configurations Δ and Λ are assigned to the isomers in the first and second fractions eluted by hexane/propanol, respectively. The assignment of the absolute configuration was based on the theoretically predicted circular dichroism in the intense ligand-exciton band at around 36×10^3 cm^{-1}. Three absorption bands of $[Ru(acac)_3]$ observed in the range of $(18-40) \times 10^3$ cm^{-1} are ascribed to the excited states, which are the configuration-interaction admixtures of the ligand-to-metal charge-transfer (LMCT) excited states and the ligand (π,π^*) excited triplets and singlets. The LMCT excited states also interact with the ground-state configurations and split the ground-state sublevels. Theory predicts that circular dichroism in the ligand (π,π^*) excitations from the lowest ground-state sublevel is reversed in this particular open-shell complex with reference to those in the ligand (π,π^*) exciton bands found for the corresponding isomers with no low-lying charge-transfer for excited states.

Introduction

$[Ru^{III}(acac)_3]$ (acac = 2,4-pentanedionate) has no ionic charge, and thus resolution of the enantiomeric isomers can not be effected by fractional precipitation with an oppositely charged resolving reagent. So far, a good number of papers have been devoted to resolutions of the optical isomers of noncharged complexes by liquid chromatography on chiral sorbent columns.[1-7] However only partial resolution has been obtained. In the present work, we achieved a complete resolution of the enantiomers of $[Ru(acac)_3]$ by high-performance liquid chromatography (HPLC) on a column of porous silica gel coated with cellulose tris(phenylcarbamate). The isomers in the first and the second fractions of elution are of configurations Δ and Λ, respectively. The present assignment is based on the theoretically predicted circular dichroism (CD) in the intense absorption band at around 36×10^3 cm^{-1}, which is predominantly characterized as the ligand (π,π^*) exciton band. The assignment, however, is also supported by the CD spectrum of partly resolved $[Ru(acac)_3]$ if the asymmetric synthesis yields the Δ isomer in excess.[8] The CD sign was reproduced with the enantiomer separated by the alternative method.[9]

Chromatographic resolution of the optical isomers of $[Co^{III}(acac)_3]$, $[Cr^{III}(acac)_3]$ and $[Al^{III}(acac)_3]$ was carried out[10] on a column of silica gel coated with (+)-poly(triphenylmethyl methacrylate).[11] The Δ isomer was in the earlier eluted fraction. In the present work, we also applied this column. However, the column showed no chiral recognition ability for $[Ru(acac)_3]$.

$[Ru(acac)_3]$ exhibits three absorption bands in the visible and ultraviolet region. These bands are attributable to the lowest excited states, which are the configuration-interaction admixtures of the ligand-to-metal charge-transfer (LMCT) excited states and the ligand (π,π^*) excited triplets and singlets with varied predominant characters. The LMCT excited states also interact with the ground-state configurations and, as a result, split the ground-state sublevels. In this particular open-shell complex, the CD sign in the ligand (π,π^*) excitation from the lowest component state of the split ground-state sublevels is reversed with reference to that of the corresponding exciton band of the complexes with no low-lying charge-transfer excited states. The closed-shell tris(β-diketonato) complexes of Δ configuration shows a negative and a positive CD band with increasing wavenumber in the ligand (π,π^*) band.[12] It was suggested that simple exciton model yields uncertainties in analysis of the CD spectra of open-shell complexes.[13] In this paper, we present a model which can reasonably describe the lowest excited states of $[Ru(acac)_3]$ and correctly reproduce the circular dichroism reversed with reference to that of the corresponding exciton band of the complexes with no low-lying charge-transfer excited states.

Experimental Section

$[Ru^{III}(acac)_3]$[14] and $[Ru^{III}(dpm)_3]$ (dpm = 2,2,6,6-tetramethyl-3,5-heptanedionate)[15] were synthesized by the literature methods with some modification.[16] $[Ru(acac)_3]$ and $[Ru(dpm)_3]$ were purified by chromatography on alumina (Merck alumina 90) columns using benzene as

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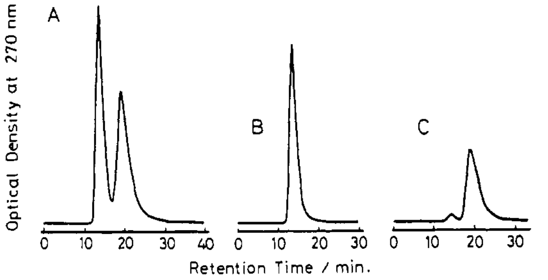

Figure 1. Chromatograms of the resolution of [$Ru(acac)_3$] on a CHIRALCEL OC column: (A) racemic mixture; (B) first eluted fraction; (C) second eluted fraction.

eluents,[16] recrystallization from methanol, and then sublimation. [$Ru^{III}(hfac)_3$] (hfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate) was prepared by oxidation of K[$Ru^{II}(hfac)_3$] with hydrogen peroxide in a benzene–water mixed medium.[16] [$Ru(hfac)_3$] isolated from the benzene layer was purified by sublimation and then stored under argon atmosphere.

[$Sc^{III}(acac)_3$],[17] [$Y^{III}(acac)_3$],[18] and [$Fe^{III}(acac)_3$][19] for comparative studies were prepared and purified by the literature methods. All the complexes used in the present work were identified by elemental analysis.

Chromatographic resolutions of [$Ru(acac)_3$], [$Ru(dpm)_3$], and [$Ru(hfac)_3$] were carried out on the columns packed with stationary chiral phase, CHIRALPAK OT(+) (poly(triphenylmethyl methacrylate)), CHIRALPAK OP(+) (poly(diphenylpyrid-2-ylmethyl methacrylate)), CHIRALCEL OB (cellulose tribenzoate), and CHIRALCEL OC (cellulose tris(phenylcarbamate)), which are commercially available from Daicel Chemical Industries, Ltd., Tokyo. [$Ru(acac)_3$] was completely resolved at room temperature on a CHIRALCEL OC column with a solution of 9 mg of [$Ru(acac)_3$] dissolved in 2 mL of a 7:1 mixed solvent of ethanol and hexane/2-propanol (9:1) and eluted by a mixture hexane/2-propanol (9:1). The resolutions of all the other Ru(III) complexes were not successful.

The enantiomers of [$Ru(acac)_3$] were separated in semipreparative scale on a CHIRALCEL OC column (0.46 cm i.d. × 25 cm length). From the elution, the solvent was removed under reduced pressure in a bath at 30 °C. The enantiomeric excess of the first fraction was 100% while that of the second was 91%, respectively. The optical purity was measured with the UV detector operated at 270 nm. It is noted that the enantiomeric excess was not changed upon condensation of the eluates and by dissolving each enantiomer in solvents and letting them stand at room temperature overnight. HPLC resolution on the stationary chiral phase column was carried out at 22 °C by using a flow rate of 1.0 mL/min by use of a JASCO BIP-I HPLC pump with Uvidec-100V variable wavelength detector.

Circular dichroism (CD) spectra were taken on a JASCO spectropolarimeter J-500C. Absorption spectra were measured on a Hitachi spectrophotometer Model 330. Luminescence emission as well as excitation spectra were taken on a Hitachi spectrofluorometer Model 850 equipped with a Hamamatsu Photonics photomultiplier Model R928. Raman spectra were obtained on a JEOL laser Raman spectrophotometer Model 400D equipped with a Hamamatsu Photonics photomultiplier Model R649 by irradiation of the lines from an NEC GLS 3300 argon ion laser. IR spectra were taken on a JEOL JIR-100 FT-IR spectrophotometer using KBr disks. Measurements of NMR were carried out on a JEOL-FX-200 FT-NMR spectrometer with reference to $CHCl_3$.

Results and Discussion

Figure 1 shows chromatograms of the resolution of enantiomeric [$Ru(acac)_3$] on a column of porous silica gel coated with cellulose tris(phenylcarbamate). The chromatogram indicates that the enantiomeric excess of the first fraction is 100% while that of the second fraction is 91%. However, another run with the second fraction yields complete resolution. Figure 2 presents the CD spectra of enantiomeric [$Ru(acac)_3$], which were isolated from the first and second fractions and then dissolved in methanol. The CD intensity of the isomer in the first fraction, $\Delta\epsilon = \epsilon_L - \epsilon_R = 43.6\ M^{-1}\ cm^{-1}$ at 275 nm. The CD intensities reproduce the values of enantiomeric excess of the respective fractions. Figure 2 also shows the absorption spectrum of [$Ru(acac)_3$] in methanol.

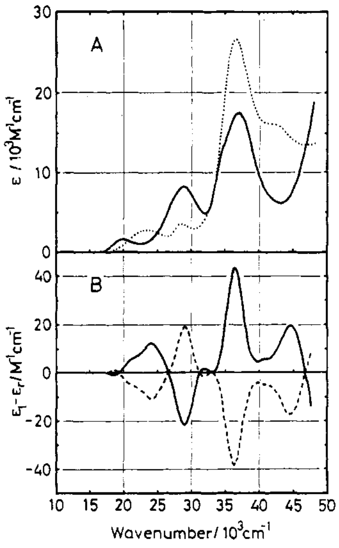

Figure 2. (A) Absorption spectra of [$Ru(acac)_3$] (—) and [$Fe(acac)_3$] (···) in methanol; (B) CD spectra of the first fraction (—) and the second fraction (---) in methanol.

The CD spectra of the first and the second fraction well correspond to those reported with partly resolved [$Ru(acac)_3$] with the Δ and Λ isomer in excess,[8,9] and also those observed for completely resolved Δ-trans,Δ-cis and Λ-trans,Λ-cis diastereomers of [Ru{(+)-atc}$_3$] ((+)-atc = (+)-3-acetyl camphorate),[20] respectively. This suggests that the isomer in the earlier-eluted fraction is of Δ conformation. However, it should be noted that the CD sign in the ligand (π,π^*) band of the diastereomers of [Ru{(+)-atc}$_3$] is reversed with reference to those of the corresponding isomers of [Cr{(+)-atc}$_3$],[21] [Co{(+)-atc}$_3$],[21] and [Rh{(+)-atc}$_3$].[22]

Four possible diastereomers A–D of [Cr{(+)-atc}$_3$],[21] [Co{(+)-atc}$_3$],[21] [Ru{(+)-atc}$_3$],[20] and [Rh{(+)-atc}$_3$][22] have been separated by thin-layer chromatography on silica gel: the multiplicity of proton NMR signals of the 3-acetylmethyl group in diastereomers A and B clearly indicates a trans arrangement of ligands (C_1 symmetry) and the single NMR signal in the same region of diastereomers C and D is consistent with a cis geometry (C_3 symmetry), while the CD spectra show that the trans isomers A and B are in opposite helicities and the same is true for the two cis isomers, C and D. The order of thin-layer chromatographic elution of diastereomers is Δ-trans > Λ-trans > Λ-cis > Δ-cis and is independent of the eluting solvents.

The Λ configuration of $(-)_{546}$-[$Co(acac)_3$] was determined with quasi-racemic monoclinic crystals obtained by crystallization of a mixture of partially resolved [$Co(acac)_3$] and racemic [$Al(acac)_3$].[23] The CD spectrum of Λ-$(-)_{546}$-[$Co(acac)_3$] exhibits a negative band at $15.5 \times 10^3\ cm^{-1}$ and a more intense, positive band at $17.5 \times 10^3\ cm^{-1}$,[24] which are ascribed to $^1A_1 \rightarrow {}^1A_2$ and $^1A_1 \rightarrow {}^1E$ components of the lowest spin-allowed (d,d*) transitions ($^1A_1 \rightarrow {}^1T_1$ in O_h), respectively, on the basis of the polarized crystal spectrum.[25] The absolute configuration of Λ-(+)-trans-[Cr{(+)-atc}$_3$] was confirmed by X-ray analysis,[26] providing a basis for the spectroscopic assignment of the Δ configuration of (−)-[$Cr(acac)_3$].[8] A single-crystal X-ray study also determined the Δ configuration of the (−)-[$Cr(acac)_3$].[27] Single-crystal spectroscopy shows that the ^4E component of the lowest (d,d*) excitation in [$Cr(acac)_3$] ($^4A_2 \rightarrow {}^4T_2$ in O_h), which exhibits a negative

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Table I. Ligand Modes of [Ru(acac)$_3$] and [Fe(acac)$_3$] in CCl$_4$ Detected by Resonance Raman (RR) Scattering upon Irradiation of the 488.0-nm Argon Ion Line

[Ru(acac)$_3$]		[Fe(acac)$_3$]		
RR, cm^{-1}	IR, cm^{-1}	RR, cm^{-1}	IR, cm^{-1}	assignt[a]
1576		1608		
	1540		1571	ν(C⋯C) + ν(C⋯O)
1366	1376 1364	1368	1389 1362	$\delta_s(CH_3)$
1274	1269	1280	1275	$\nu(C-CH_3)$ + ν(C⋯C)
1029	1018	1030	1023	$\delta_r(CH_3)$

[a] Assignments are based on the IR-active (A$_2$,E) modes of [Fe(acac)$_3$].[29]

CD band for the Δ configuration, lies at higher energy.[28] The Δ configurations of [Cr(acac)$_3$] and [Co(acac)$_3$] exhibit a positive and a negative CD band with increasing wavenumber in the lowest ligand field (d,d*) band. It should be noted that the isomer in the earlier eluted fraction of [Ru(acac)$_3$], which is assigned as Δ configuration, shows a negative and a positive CD band with increasing wavenumber in the lowest weak band at around 19 × 10^3 cm^{-1}.

[Ru(acac)$_3$] ($S = {}^1/_2$) and [Fe(acac)$_3$] ($S = {}^5/_2$) exhibit analogous absorption spectra regardless of the difference in spin state of the central metal d^5 systems. Therefore the absorption bands can not be ascribed to the ligand field (d,d*) transition.

Resonance Raman modes measured taken by irradiation of the 488.0- and 514.5-nm argon ion lines in the first visible weak band of [Ru(acac)$_3$] as well as [Fe(acac)$_3$] correspond well to the IR-detected ligand modes of [Fe(acac)$_3$][29] as presented in Table I. The A$_1$ and E modes in the tris-chelate complex of D_3 symmetry are Raman active, while the A$_2$ and E modes are IR active. However, the Raman active modes are not so much different in frequencies from those of the IR active modes. It should be noted a participation of the π-electron system of ligand in the first visible band which is weak but still more intense than that of the normal spin-allowed (d,d*) transitions.

Suppose a Ru(III) ion in an octahedral ligand field of ΔE ($\equiv E(d_\sigma) - E(d_\pi)$) = 28 × 10^3 cm^{-1}, which is assumed to be comparable to $[Ru(H_2O)_6]^{3+}$,[30] so that theory predicts that the ground state is in a spin-doublet state ($^2T_2$) and a series of low-lying (d,d*) transitions ($^4T_1$, 16.4 × 10^3 cm^{-1}; $^4T_2$, 21.0 × 10^3 cm^{-1}; $^6A_1$, 24.3 × 10^3 cm^{-1}; $^2A_2$, 24.8 × 10^3 cm^{-1}; $^2T_1$, 25.1 × 10^3 cm^{-1}, ^2E, 28.03 × 10^3 cm^{-1}; $^2A_1$, 36.1 × 10^3 cm^{-1}), assuming that $C = 4B$ and B = 600 cm^{-1}.[30] This suggests that the spin-allowed ligand-field excited states of [Ru(acac)$_3$] are energetically higher than the excited states corresponding to the first visible weak band. An IR band observed near 4000 cm^{-1} is not ascribed to the ligand field excitation but to the electronic excitation within the ground doublet $^2T_2$.[31] On the other hand, there should be no corresponding spin-allowed ligand field transitions in [Fe(acac)$_3$]. A reduced value of ΔE (=14.5 × 10^3 cm^{-1}) yields the sextet ground state of the Fe(III) analogue ($^6A_1$) and the spin-forbidden excited states ($^4T_1$, 8.7 × 10^3 cm^{-1}; $^4T_2$, 13.4 × 10^3 cm^{-1}). In fact, very weak bands are observed with [Fe(acac)$_3$] at 9.8 × 10^3 cm^{-1} (ϵ = 0.4) and 13.3 × 10^3 cm^{-1} (ϵ = 1.2), which have been assigned to the spin-forbidden transitions $^6A_1 \rightarrow {}^4T_1$ and $^6A_1 \rightarrow {}^4T_2$, respectively.[32]

NMR spectra of [Ru(acac)$_3$] and [Fe(acac)$_3$] in CDCl$_3$ at 20 °C exhibit paramagnetic shifts corresponding to the spin doublet and sextet, respectively ([Ru(acac)$_3$], $\delta(-CH_3) = -5.7$, $\delta(-CH{=}) = -30.7$; [Fe(acac)$_3$], $\delta(-CH_3) = 21.8$, $\delta(-CH{=}) = -30.0$). Raw data for the NMR spectra are presented in Figure A1 of the supplemental material. The spin states were also determined by susceptibility measurements.[33,34]

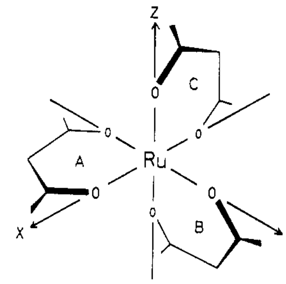

Figure 3. Molecular coordinates of Δ-[Ru(acac)$_3$].

Absorption spectra of [Ru(acac)$_3$] and [Fe(acac)$_3$] are described by a superposition of the ligand-to-metal charge-transfer excited states and the ligand β-diketonate (π,π^*) excited triplets and singlets. Suppose a Δ conformer set in a coordinate system illustrated in Figure 3; the zero-order ground-doublet wave functions are given as

$$\begin{aligned}
|0,\zeta,S = \tfrac{1}{2}\rangle &= |\psi_A\bar{\psi}_A\psi_B\bar{\psi}_B\psi_C\bar{\psi}_C\xi\bar{\xi}\eta\bar{\eta}\zeta| \\
|0,\xi,S = \tfrac{1}{2}\rangle &= |\psi_A\bar{\psi}_A\psi_B\bar{\psi}_B\psi_C\bar{\psi}_C\eta\bar{\eta}\zeta\bar{\zeta}\xi| \\
|0,\eta,S = \tfrac{1}{2}\rangle &= |\psi_A\bar{\psi}_A\psi_B\bar{\psi}_B\psi_C\bar{\psi}_C\zeta\bar{\zeta}\xi\bar{\xi}\eta|
\end{aligned} \tag{1}$$

where ψ_A, ψ_B and ψ_C are the highest filled π molecular orbitals of ligands A, B, and C, which are symmetric with respect to symmetry operation $\hat{\sigma}_v$ within the individual ligands, ψ_A and $\bar{\psi}_A$ indicate the occupation of α spin and β spin, and η, ξ, and ζ are the conventionally defined d_π orbitals.[35] Here the zero-order ground state of ruthenium(III) d^5 ion is assumed to be the $^2T_2$ state in an octahedral ligand field.

The ligand-to-metal charge-transfer (LMCT) excited configurations are spin doublets:

$$\begin{aligned}
|CT_A,S = \tfrac{1}{2}\rangle &= |\psi_B\bar{\psi}_B\psi_C\bar{\psi}_C\psi_A\xi\bar{\xi}\eta\bar{\eta}\zeta\bar{\zeta}| \\
|CT_B,S = \tfrac{1}{2}\rangle &= |\psi_C\bar{\psi}_C\psi_A\bar{\psi}_A\psi_B\xi\bar{\xi}\eta\bar{\eta}\zeta\bar{\zeta}| \\
|CT_C,S = \tfrac{1}{2}\rangle &= |\psi_A\bar{\psi}_A\psi_B\bar{\psi}_B\psi_C\xi\bar{\xi}\eta\bar{\eta}\zeta\bar{\zeta}|
\end{aligned} \tag{2}$$

The energies of the LMCT states are parametrized as Δ_{CT}. There are other excited doublets that originate from the ligand $^3(\pi,\pi^*)$ and $^1(\pi,\pi^*)$ excited states. The wave functions are shown only with the highest S_z component of the ligand A-localized excited states:

$$\begin{aligned}
|^3A,\zeta,S = \tfrac{3}{2}\rangle &= |\psi_A\chi_A\psi_B\bar{\psi}_B\psi_C\bar{\psi}_C\xi\bar{\xi}\eta\bar{\eta}\zeta| \\
|^3A,\xi,S = \tfrac{3}{2}\rangle &= |\psi_A\chi_A\psi_B\bar{\psi}_B\psi_C\bar{\psi}_C\eta\bar{\eta}\zeta\bar{\zeta}\xi| \\
|^3A,\eta,S = \tfrac{3}{2}\rangle &= |\psi_A\chi_A\psi_B\bar{\psi}_B\psi_C\bar{\psi}_C\zeta\bar{\zeta}\xi\bar{\xi}\eta|
\end{aligned} \tag{3}$$

$$\begin{aligned}
|^3A,\zeta,S = \tfrac{1}{2}\rangle = (1/6^{1/2})\{&-2|\psi_A\chi_A\psi_B\bar{\psi}_B\psi_C\bar{\psi}_C\xi\bar{\xi}\eta\bar{\eta}\bar{\zeta}| + \\
&|\psi_A\bar{\chi}_A\psi_B\bar{\psi}_B\psi_C\bar{\psi}_C\xi\bar{\xi}\eta\bar{\eta}\zeta| + |\bar{\psi}_A\chi_A\psi_B\bar{\psi}_B\psi_C\bar{\psi}_C\xi\bar{\xi}\eta\bar{\eta}\zeta|\} \\
|^3A,\xi,S = \tfrac{1}{2}\rangle = (1/6^{1/2})\{&-2|\psi_A\chi_A\psi_B\bar{\psi}_B\psi_C\bar{\psi}_C\eta\bar{\eta}\zeta\bar{\zeta}\bar{\xi}| + \\
&|\psi_A\bar{\chi}_A\psi_B\bar{\psi}_B\psi_C\bar{\psi}_C\eta\bar{\eta}\zeta\bar{\zeta}\xi| + |\bar{\psi}_A\chi_A\psi_B\bar{\psi}_B\psi_C\bar{\psi}_C\eta\bar{\eta}\zeta\bar{\zeta}\xi|\} \\
|^3A,\eta,S = \tfrac{1}{2}\rangle = (1/6^{1/2})\{&-2|\psi_A\chi_A\psi_B\bar{\psi}_B\psi_C\bar{\psi}_C\zeta\bar{\zeta}\xi\bar{\xi}\bar{\eta}| + \\
&|\psi_A\bar{\chi}_A\psi_B\bar{\psi}_B\psi_C\bar{\psi}_C\zeta\bar{\zeta}\xi\bar{\xi}\eta| + |\bar{\psi}_A\chi_A\psi_B\bar{\psi}_B\psi_C\bar{\psi}_C\zeta\bar{\zeta}\xi\bar{\xi}\eta|\}
\end{aligned} \tag{4}$$

$$\begin{aligned}
&|^1A,\zeta,S = \tfrac{1}{2}\rangle = \\
&\quad (1/2^{1/2})\{|\psi_A\bar{\chi}_A\psi_B\bar{\psi}_B\psi_C\bar{\psi}_C\xi\bar{\xi}\eta\bar{\eta}\zeta| - |\bar{\psi}_A\chi_A\psi_B\bar{\psi}_B\psi_C\bar{\psi}_C\xi\bar{\xi}\eta\bar{\eta}\zeta|\} \\
&|^1A,\xi,S = \tfrac{1}{2}\rangle = \\
&\quad (1/2^{1/2})\{|\psi_A\bar{\chi}_A\psi_B\bar{\psi}_B\psi_C\bar{\psi}_C\eta\bar{\eta}\zeta\bar{\zeta}\xi| - |\bar{\psi}_A\chi_A\psi_B\bar{\psi}_B\psi_C\bar{\psi}_C\eta\bar{\eta}\zeta\bar{\zeta}\xi|\} \\
&|^1A,\eta,S = \tfrac{1}{2}\rangle = \\
&\quad (1/2^{1/2})\{|\psi_A\bar{\chi}_A\psi_B\bar{\psi}_B\psi_C\bar{\psi}_C\zeta\bar{\zeta}\xi\bar{\xi}\eta| - |\bar{\psi}_A\chi_A\psi_B\bar{\psi}_B\psi_C\bar{\psi}_C\zeta\bar{\zeta}\xi\bar{\xi}\eta|\}
\end{aligned} \tag{5}$$

where $^{1,3}A(\equiv{}^{1,3}(\psi_A \leftarrow \chi_A))$ are the lowest (π,π^*) excited singlet

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and triplet excited states localized on ligand A and χ_A is the lowest vacant π orbital of ligand A, which is antisymmetric with respect to symmetry operations $\hat{\sigma}_v$. There are analogous excited states that arise from the corresponding $^{1,3}(\pi,\pi^*)$ excitations localized on ligand B and C. Energies of these excited states are given by

$$E(^3\mathrm{A},\zeta,S={}^3\!/_2) = E(^3\mathrm{B},\xi,S={}^3\!/_2) = E(^3\mathrm{C},\eta,S={}^3\!/_2) = \Delta_\pi + 2[K-K'] \quad (6)$$

$$E(^3\mathrm{A},\xi,S={}^3\!/_2) = E(^3\mathrm{A},\eta,S={}^3\!/_2) = E(^3\mathrm{B},\eta,S={}^3\!/_2) = E(^3\mathrm{B},\zeta,S={}^3\!/_2) = E(^3\mathrm{C},\zeta,S={}^3\!/_2) = E(^3\mathrm{C},\xi,S={}^3\!/_2) = \Delta_\pi + K - 2K'$$

$$E(^3\mathrm{A},\zeta,S={}^1\!/_2) = E(^3\mathrm{B},\xi,S={}^1\!/_2) = E(^3\mathrm{C},\eta,S={}^1\!/_2) = \Delta_\pi + 2[K-K'] \quad (7)$$

$$E(^3\mathrm{A},\xi,S={}^1\!/_2) = E(^3\mathrm{A},\eta,S={}^1\!/_2) = E(^3\mathrm{B},\eta,S={}^1\!/_2) = E(^3\mathrm{B},\zeta,S={}^1\!/_2) = E(^3\mathrm{C},\zeta,S={}^1\!/_2) = E(^3\mathrm{C},\xi,S={}^1\!/_2) = \Delta_\pi + {}^5\!/_2K - {}^1\!/_2K'$$

$$E(^1\mathrm{A},\zeta,S={}^1\!/_2) = E(^1\mathrm{B},\xi,S={}^1\!/_2) = E(^1\mathrm{C},\eta,S={}^1\!/_2) = \Delta_\pi + 2K_\pi + 2[K-K'] \quad (8)$$

$$E(^1\mathrm{A},\xi,S={}^1\!/_2) = E(^1\mathrm{A},\eta,S={}^1\!/_2) = E(^1\mathrm{B},\eta,S={}^1\!/_2) = E(^1\mathrm{B},\zeta,S={}^1\!/_2) = E(^1\mathrm{C},\zeta,S={}^1\!/_2) = E(^1\mathrm{C},\xi,S={}^1\!/_2) = \Delta_\pi + 2K_\pi + {}^3\!/_2[K-K']$$

where Δ_π is the energy of the lowest ligand (π,π^*) excited triplet and $(\psi_A\chi_A|\chi_A\psi_A) = K_\pi$, $(\psi_A\xi|\xi\psi_A) = (\psi_A\eta|\eta\psi_A) = K$, and $(\chi_A\xi|\xi\chi_A) = (\chi_A\eta|\eta\chi_A) = K'$ are non-zero exchange interactions, while $(\psi_A\zeta|\zeta\psi_A)$ and $(\chi_A\zeta|\zeta\chi_A)$ are negligibly small because of no sizable overlap of ψ_A, χ_A and ζ.

It should be noted that there is an exciton coupling between $|^{1,3}\mathrm{A},\zeta\rangle$ and $|^{1,3}\mathrm{B},\zeta\rangle$. The interaction is described as

$$\langle ^{1,3}\mathrm{A},\zeta|\hat{H}|^{1,3}\mathrm{B},\zeta\rangle = -(\chi_A\chi_B|\psi_B\psi_A) + \binom{2}{0}(\chi_A\psi_A|\psi_B\chi_B) \quad (9)$$

where $(\chi_A\chi_B|\psi_B\psi_A)$ is a Coulomb interaction between overlap charges $(\chi_A\chi_B)$, and $(\psi_B\psi_A)$ and $(\chi_A\psi_A|\psi_B\chi_B)$ is the interaction between transition charges $(\chi_A\psi_A)$ and $(\psi_B\chi_B)$, and 2 and 0 in $\binom{2}{0}$ stand for the singlet and the triplet, respectively. The overlap charges between two different ligands are so small that $(\chi_A\chi_B|\psi_B\psi_A)$ can be ignored. Thus the exciton coupling interactions are nonzero only for the singlets:

$$\langle ^1\mathrm{A},\zeta|\hat{H}|^1\mathrm{B},\zeta\rangle = \langle ^1\mathrm{B},\zeta|\hat{H}|^1\mathrm{C},\zeta\rangle = \langle ^1\mathrm{C},\zeta|\hat{H}|^1\mathrm{A},\zeta\rangle = \langle ^1\mathrm{A},\xi|\hat{H}|^1\mathrm{B},\xi\rangle = \langle ^1\mathrm{B},\xi|\hat{H}|^1\mathrm{C},\xi\rangle = \langle ^1\mathrm{C},\xi|\hat{H}|^1\mathrm{A},\xi\rangle = \langle ^1\mathrm{A},\eta|\hat{H}|^1\mathrm{B},\eta\rangle = \langle ^1\mathrm{B},\eta|\hat{H}|^1\mathrm{C},\eta\rangle = \langle ^1\mathrm{C},\eta|\hat{H}|^1\mathrm{A},\eta\rangle = 2(\chi_A\psi_A|\psi_B\chi_B) = 2K_{AB} \quad (10)$$

The highest filled orbitals $\psi_{A,B,C}$ and the lowest vacant orbitals $\chi_{A,B,C}$ make an overlap with metal d_π orbitals. This gives rise to the configuration-interaction admixings of the LMCT excited configurations with the ground-state doublets and the ligand-localized $^{1,3}(\pi,\pi^*)$ excited doublets. The interactions are given as follows:

$$\langle \mathrm{CT_A}|\hat{H}|0,\zeta\rangle = -(\zeta|\hat{H}|\psi_A) = 0$$

$$\langle \mathrm{CT_A}|\hat{H}|0,\xi\rangle = -(\xi|\hat{H}|\psi_A) = Y \quad (11)$$

$$\langle \mathrm{CT_A}|\hat{H}|0,\eta\rangle = -(\eta|\hat{H}|\psi_A) = -Y$$

$$\langle \mathrm{CT_A}|\hat{H}|^3\mathrm{A},\zeta\rangle = (-6^{1/2}/2)(\zeta|\hat{H}|\chi_A) = 0$$

$$\langle \mathrm{CT_A}|\hat{H}|^3\mathrm{A},\xi\rangle = (-6^{1/2}/2)(\xi|\hat{H}|\chi_A) = (-6^{1/2}/2)X$$

$$\langle \mathrm{CT_A}|\hat{H}|^3\mathrm{A},\eta\rangle = (-6^{1/2}/2)(\eta|\hat{H}|\chi_A) = (-6^{1/2}/2)X \quad (12)$$

$$\langle \mathrm{CT_A}|\hat{H}|^1\mathrm{A},\zeta\rangle = (-2^{1/2}/2)(\zeta|\hat{H}|\chi_A) = 0$$

$$\langle \mathrm{CT_A}|\hat{H}|^1\mathrm{A},\xi\rangle = (-2^{1/2}/2)(\xi|\hat{H}|\chi_A) = (-2^{1/2}/2)X$$

$$\langle \mathrm{CT_A}|\hat{H}|^1\mathrm{A},\eta\rangle = (-2^{1/2}/2)(\eta|\hat{H}|\chi_A) = (-2^{1/2}/2)X$$

where $(d_\pi|\hat{H}|\psi_A)$ and $(d_\pi|\hat{H}|\chi_A)$ are the one-electron interactions of overlapping orbitals, which are parametrized as Y and X, respectively. There are the corresponding interactions with ^{1,3}B and ^{1,3}C. The one-electron interactions are summarized in the following matrix:

$$\begin{array}{ccccccc} & \psi_A & \psi_B & \psi_C & \chi_A & \chi_B & \chi_C \\ \zeta & 0 & Y & -Y & 0 & X & X \\ \xi & -Y & 0 & Y & X & 0 & X \\ \eta & Y & -Y & 0 & X & X & 0 \end{array}$$

Table II presents the symmetry-based wave functions, diagonal energies, and off-diagonal interactions of the ground-state and the lowest excited-state doublet configurations of $[\mathrm{Ru(acac)_3}]$.

In the present work, it is assumed that the ligand $^1(\pi,\pi^*)$ excitations are exclusively allowed and grant intensities to the LMCT excited states by the configuration interactions. The nonzero transition moments are

$$\langle ^1\mathrm{A},\zeta|\hat{\mathbf{m}}|0,\zeta\rangle = \langle ^1\mathrm{A},\xi|\hat{\mathbf{m}}|0,\xi\rangle = \langle ^1\mathrm{A},\eta|\hat{\mathbf{m}}|0,\eta\rangle = 2^{1/2}(\chi_A|\hat{\mathbf{m}}|\psi_A) = 2^{1/2}M(1/2^{1/2})[\mathbf{i}+\mathbf{j}]$$

$$\langle ^1\mathrm{B},\zeta|\hat{\mathbf{m}}|0,\zeta\rangle = \langle ^1\mathrm{B},\xi|\hat{\mathbf{m}}|0,\xi\rangle = \langle ^1\mathrm{B},\eta|\hat{\mathbf{m}}|0,\eta\rangle = 2^{1/2}M(1/2^{1/2})[\mathbf{j}+\mathbf{k}]$$

$$\langle ^1\mathrm{C},\zeta|\hat{\mathbf{m}}|0,\zeta\rangle = \langle ^1\mathrm{C},\xi|\hat{\mathbf{m}}|0,\xi\rangle = \langle ^1\mathrm{C},\eta|\hat{\mathbf{m}}|0,\eta\rangle = 2^{1/2}M(1/2^{1/2})[\mathbf{k}+\mathbf{i}]$$

$$\langle \mathrm{CT_A}|\hat{\mathbf{m}}|\mathrm{CT_A}\rangle = -eR'(1/2^{1/2})[\mathbf{i}-\mathbf{j}] \quad (13)$$

$$\langle \mathrm{CT_B}|\hat{\mathbf{m}}|\mathrm{CT_B}\rangle = -eR'(1/2^{1/2})[\mathbf{j}-\mathbf{k}]$$

$$\langle \mathrm{CT_C}|\hat{\mathbf{m}}|\mathrm{CT_C}\rangle = -eR'(1/2^{1/2})[\mathbf{k}-\mathbf{i}]$$

and

$$\langle ^1\mathrm{A},\zeta|\hat{\mu}|0,\zeta\rangle = \langle ^1\mathrm{A},\xi|\hat{\mu}|0,\xi\rangle = \langle ^1\mathrm{A},\eta|\hat{\mu}|0,\eta\rangle = 2^{1/2}(\chi_A|\hat{\mu}|\psi_A) = 2^{1/2}iaM\,\mathbf{k} \quad (14)$$

$$\langle ^1\mathrm{B},\zeta|\hat{\mu}|0,\zeta\rangle = \langle ^1\mathrm{B},\xi|\hat{\mu}|0,\xi\rangle = \langle ^1\mathrm{B},\eta|\hat{\mu}|0,\eta\rangle = 2^{1/2}iaM\,\mathbf{i}$$

$$\langle ^1\mathrm{C},\zeta|\hat{\mu}|0,\zeta\rangle = \langle ^1\mathrm{C},\xi|\hat{\mu}|0,\xi\rangle = \langle ^1\mathrm{C},\eta|\hat{\mu}|0,\eta\rangle = 2^{1/2}iaM\,\mathbf{j}$$

where $\hat{\mathbf{m}}$ and $\hat{\mu}$ are the electric and magnetic dipole operators ($\hat{\mathbf{m}} = \sum e\hat{\mathbf{r}}$, $\hat{\mu} = \mu_B\sum\hat{\mathbf{r}}\otimes\hat{\mathbf{p}}/\hbar$), R' is the position of the center of $\langle \mathrm{a}|\hat{\mathbf{m}}|\mathrm{a}\rangle$, and $\mathbf{i}$, $\mathbf{j}$, $\mathbf{k}$ are the unit vectors in the direction of the x, y, z axes. The magnetic dipole transition moment $\langle \mathrm{j}|\hat{\mu}|\mathrm{a}\rangle$ is rewritten in terms of the electric dipole transition moment $\langle \mathrm{j}|\hat{\mathbf{m}}|\mathrm{a}\rangle$ localized on each of the ligands such as

$$i\mu_B\frac{m}{e\hbar^2}(E_j - E_a)\mathbf{R}\otimes\langle \mathrm{j}|\hat{\mathbf{m}}|\mathrm{a}\rangle$$

where E_j and E_a are the energies of the states $|\mathrm{j}\rangle$ and $|\mathrm{a}\rangle$ and $\mathbf{R}$ is the position vector of the center of $\langle \mathrm{j}|\hat{\mathbf{m}}|\mathrm{a}\rangle$. The transition moments between the ground-state and the lowest excited-state configurations are summarized in Table A1 of the supplemental material.

Suppose a diamagnetic complex in Δ configuration with no low-lying MLCT and/or LMCT excited states; the rotatory strengths are given by

$$R((1/3^{1/2})\{^1\mathrm{A} + {}^1\mathrm{B} + {}^1\mathrm{C}\}) = 2(2^{1/2})aM^2$$

$$R((1/6^{1/2})\{2\,^1\mathrm{A} - {}^1\mathrm{B} - {}^1\mathrm{C}\}) = -2^{1/2}aM^2 \quad (15)$$

$$R((1/2^{1/2})\{^1\mathrm{B} - {}^1\mathrm{C}\}) = -2^{1/2}aM^2$$

for the exciton states $(1/3^{1/2})\{^1\mathrm{A} + {}^1\mathrm{B} + {}^1\mathrm{C}\}$ at $\Delta_\pi + 2K_\pi + 4K_{AB}$ and $(1/6^{1/2})\{2\,^1\mathrm{A} - {}^1\mathrm{B} - {}^1\mathrm{C}\}$, $(1/2^{1/2})\{^1\mathrm{B} - {}^1\mathrm{C}\}$ at $\Delta_\pi + 2K_\pi - 2K_{AB}$, respectively. This implies that negative and a positive CD bands appear at $\Delta_\pi + 2K_\pi - 2K_{AB}$ and $\Delta_\pi + 2K_\pi + 4K_{AB}$ in the ligand $^1(\pi,\pi^*)$ excitation. In fact, the Δ conformer such as Δ-$[\mathrm{Si(acac)_3}]^+$ exhibits this type of CD spectrum.[12]

From the spectra of the diamagnetic trivalent metal complexes with no low-lying charge-transfer excited states shown in Figure 4, we determined $\Delta_\pi = 24 \times 10^3$ cm^{-1}, $K_\pi = 4.5 \times 10^3$ cm^{-1}, $M = 1.02ea_0$ so as to reproduce the energies of the lowest (π,π^*) excited triplet and singlet of coordinated β-diketonate and the

Table II. Wave Functions, Diagonal Energies, and Interactions of the Ground-State and the Lowest Excited-State Configurations

$\vert 0,1\rangle$ $\vert 0,2\rangle$	$\vert \mathrm{CT},1\rangle$ $\vert \mathrm{CT},2\rangle$	$\vert {}^3\psi_1,1\rangle$ $\vert {}^3\psi_1,2\rangle$	$\vert {}^3\psi_2,1\rangle$ $\vert {}^3\psi_2,2\rangle$	$\vert {}^3\psi_3,1\rangle$ $\vert {}^3\psi_3,2\rangle$	$\vert {}^1\psi_1,1\rangle$ $\vert {}^1\psi_1,2\rangle$	$\vert {}^1\psi_2,1\rangle$ $\vert {}^1\psi_2,2\rangle$	$\vert {}^1\psi_3,1\rangle$ $\vert {}^1\psi_3,2\rangle$
0	$3^{1/2}Y$	0	0	0	0	0	0
	Δ_{CT}	$-3^{1/2}X$	0	0	$-X$	0	0
		$\Delta_\pi + {}^5/_2K - {}^1/_2K'$	0	0	0	0	0
			$\Delta_\pi + {}^5/_2K - {}^1/_2K'$	0	0	0	0
				$\Delta_\pi + 2K - 2K'$	0	0	0
					$\Delta_\pi + 2K_\pi + {}^3/_2K - {}^3/_2K' - K_{\mathrm{AB}}$	$3^{1/2}K_{\mathrm{AB}}$	$2^{1/2}K_{\mathrm{AB}}$
						$\Delta_\pi + 2K_\pi + {}^3/_2K - {}^3/_2K' + K_{\mathrm{AB}}$	$6^{1/2}K_{\mathrm{AB}}$
							$\Delta_\pi + 2K_\pi + 2K - 2K'$

$\vert 0,1\rangle = (1/6^{1/2})\{2\vert 0,\zeta\rangle - \vert 0,\xi\rangle - \vert 0,\eta\rangle\}$; $\vert 0,2\rangle = (1/2^{1/2})\{\vert 0,\xi\rangle - \vert 0,\eta\rangle\}$

$\vert \mathrm{CT},1\rangle = (1/2^{1/2})\{-\vert \mathrm{CT_B}\rangle + \vert \mathrm{CT_C}\rangle\}$; $\vert \mathrm{CT},2\rangle = (1/6^{1/2})\{2\vert \mathrm{CT_A}\rangle - \vert \mathrm{CT_B}\rangle - \vert \mathrm{CT_C}\rangle\}$

$\vert {}^3\psi_1,1\rangle = {}^1/_2\{-\vert {}^3\mathrm{B},\zeta\rangle + \vert {}^3\mathrm{C},\zeta\rangle + \vert {}^3\mathrm{C},\xi\rangle - \vert {}^3\mathrm{B},\eta\rangle\}$, $\vert {}^3\psi_2,1\rangle = (1/12^{1/2})\{\vert {}^3\mathrm{B},\zeta\rangle - \vert {}^3\mathrm{C},\zeta\rangle + 2\vert {}^3\mathrm{A},\xi\rangle + \vert {}^3\mathrm{C},\xi\rangle - 2\vert {}^3\mathrm{A},\eta\rangle - \vert {}^3\mathrm{B},\eta\rangle\}$, $\vert {}^3\psi_3,1\rangle = (1/2^{1/2})\{\vert {}^3\mathrm{B},\xi\rangle - \vert {}^3\mathrm{C},\eta\rangle\}$; $\vert {}^3\psi_1,2\rangle = (1/12^{1/2})\{\vert {}^3\mathrm{B},\zeta\rangle + \vert {}^3\mathrm{C},\zeta\rangle - 2\vert {}^3\mathrm{A},\xi\rangle + \vert {}^3\mathrm{C},\xi\rangle - 2\vert {}^3\mathrm{A},\eta\rangle + \vert {}^3\mathrm{B},\eta\rangle\}$, $\vert {}^3\psi_2,2\rangle = {}^1/_2\{-\vert {}^3\mathrm{B},\zeta\rangle - \vert {}^3\mathrm{C},\zeta\rangle + \vert {}^3\mathrm{C},\xi\rangle + \vert {}^3\mathrm{B},\eta\rangle\}$, $\vert {}^3\psi_3,2\rangle = (1/6^{1/2})\{-2\vert {}^3\mathrm{A},\zeta\rangle + \vert {}^3\mathrm{B},\xi\rangle + \vert {}^3\mathrm{C},\eta\rangle\}$

$\vert {}^1\psi_1,1\rangle = {}^1/_2\{-\vert {}^1\mathrm{B},\zeta\rangle + \vert {}^1\mathrm{C},\zeta\rangle + \vert {}^1\mathrm{C},\xi\rangle - \vert {}^1\mathrm{B},\eta\rangle\}$, $\vert {}^1\psi_2,1\rangle = (1/12^{1/2})\{\vert {}^1\mathrm{B},\zeta\rangle - \vert {}^1\mathrm{C},\zeta\rangle + 2\vert {}^1\mathrm{A},\xi\rangle + \vert {}^1\mathrm{C},\xi\rangle - 2\vert {}^1\mathrm{A},\eta\rangle - \vert {}^1\mathrm{B},\eta\rangle\}$, $\vert {}^1\psi_3,1\rangle = (1/2^{1/2})\{\vert {}^1\mathrm{B},\xi\rangle - \vert {}^1\mathrm{C},\eta\rangle\}$; $\vert {}^1\psi_1,2\rangle = -(1/12^{1/2})\{\vert {}^1\mathrm{B},\zeta\rangle + \vert {}^1\mathrm{C},\zeta\rangle - 2\vert {}^1\mathrm{A},\xi\rangle + \vert {}^1\mathrm{C},\xi\rangle - 2\vert {}^1\mathrm{A},\eta\rangle + \vert {}^1\mathrm{B},\eta\rangle\}$, $\vert {}^1\psi_2,2\rangle = {}^1/_2\{-\vert {}^1\mathrm{B},\zeta\rangle - \vert {}^1\mathrm{C},\zeta\rangle + \vert {}^1\mathrm{C},\xi\rangle + \vert {}^1\mathrm{B},\eta\rangle\}$, $\vert {}^1\psi_3,2\rangle = (1/6^{1/2})\{-2\vert {}^1\mathrm{A},\zeta\rangle + \vert {}^1\mathrm{B},\xi\rangle + \vert {}^1\mathrm{C},\eta\sigma\rangle\}$

$\vert 0,3\rangle$	$\vert \mathrm{CT},3\rangle$	$\vert {}^3\psi_1,3\rangle$	$\vert {}^3\psi_2,3\rangle$	$\vert {}^3\psi_3,3\rangle$	$\vert {}^1\psi_1,3\rangle$	$\vert {}^1\psi_2,3\rangle$	$\vert {}^1\psi_3,3\rangle$
0	0	0	0	0	0	0	0
	Δ_{CT}	$-3^{1/2}X$	0	0	$-X$	0	0
		$\Delta_\pi + {}^5/_2K - {}^1/_2K'$	0	0	0	0	0
			$\Delta_\pi + {}^5/_2K - {}^1/_2K'$	0	0	0	0
				$\Delta_\pi + 2K - 2K'$	0	0	0
					$\Delta_\pi + 2K_\pi + {}^3/_2K - {}^3/_2K' + 2K_{\mathrm{AB}}$	0	$2(2^{1/2})K_{\mathrm{AB}}$
						$\Delta_\pi + 2K_\pi + {}^3/_2K - {}^3/_2K' - 2K_{\mathrm{AB}}$	0
							$\Delta_\pi + 2K_\pi + 2K - 2K'$

$\vert 0,3\rangle = (1/3^{1/2})\{\vert 0,\zeta\rangle + \vert 0,\xi\rangle + \vert 0,\eta\rangle\}$

$\vert \mathrm{CT},3\rangle = (1/3^{1/2})\{\vert \mathrm{CT_A}\rangle + \vert \mathrm{CT_B}\rangle + \vert \mathrm{CT_C}\rangle\}$

$\vert {}^3\psi_1,3\rangle = (1/6^{1/2})\{\vert {}^3\mathrm{B},\zeta\rangle + \vert {}^3\mathrm{C},\zeta\rangle + \vert {}^3\mathrm{A},\xi\rangle + \vert {}^3\mathrm{C},\xi\rangle + \vert {}^3\mathrm{A},\eta\rangle + \vert {}^3\mathrm{B},\eta\rangle\}$, $\vert {}^3\psi_2,3\rangle = (1/6^{1/2})\{\vert {}^3\mathrm{B},\zeta\rangle - \vert {}^3\mathrm{C},\zeta\rangle - \vert {}^3\mathrm{A},\xi\rangle + \vert {}^3\mathrm{C},\xi\rangle + \vert {}^3\mathrm{A},\eta\rangle - \vert {}^3\mathrm{B},\eta\rangle\}$, $\vert {}^3\psi_3,3\rangle = (1/3^{1/2})\{\vert {}^3\mathrm{A},\zeta\rangle + \vert {}^3\mathrm{B},\xi\rangle + \vert {}^3\mathrm{C},\eta\rangle\}$

$\vert {}^1\psi_1,3\rangle = (1/6^{1/2})\{\vert {}^1\mathrm{B},\zeta\rangle + \vert {}^1\mathrm{C},\zeta\rangle + \vert {}^1\mathrm{A},\xi\rangle + \vert {}^1\mathrm{C},\xi\rangle + \vert {}^1\mathrm{A},\eta\rangle + \vert {}^1\mathrm{B},\eta\rangle\}$, $\vert {}^1\psi_2,3\rangle = (1/6^{1/2})\{\vert {}^1\mathrm{B},\zeta\rangle - \vert {}^1\mathrm{C},\zeta\rangle - \vert {}^1\mathrm{A},\xi\rangle + \vert {}^1\mathrm{C},\xi\rangle + \vert {}^1\mathrm{A},\eta\rangle - \vert {}^1\mathrm{B},\eta\rangle\}$, $\vert {}^1\psi_3,3\rangle = (1/3^{1/2})\{\vert {}^1\mathrm{A},\zeta\rangle + \vert {}^1\mathrm{B},\xi\rangle + \vert {}^1\mathrm{C},\eta\rangle\}$

Table III. Calculated Energies, Wave Functions, Transition Moments, and Rotatory Strengths of Δ-[Ru(acac)$_3$]

excited state no.[a]	energy, 10^3 cm^{-1}	wave function	transition moment, $(ea_0)^2$	rotatory strength, $ea_0\ \mu_B$
1	−1.050	$-0.9792\vert 0,1\rangle - 0.1979\vert \mathrm{CT},1\rangle + 0.0407\vert {}^3\psi_1,1\rangle + 0.0183\vert {}^1\psi_1,1\rangle - 0.0005\vert {}^1\psi_2,1\rangle - 0.0004\vert {}^1\psi_3,1\rangle$		
2	−1.050	$-0.9792\vert 0,2\rangle - 0.1979\vert \mathrm{CT},2\rangle + 0.0407\vert {}^3\psi_1,2\rangle + 0.0183\vert {}^1\psi_1,2\rangle - 0.0005\vert {}^1\psi_2,2\rangle - 0.0004\vert {}^1\psi_3,2\rangle$		
3	0.0	$1.0000\vert 0,3\rangle$	0.0	0.0
4	19.535	$0.6605\vert \mathrm{CT},3\rangle - 0.7357\vert {}^3\psi_1,3\rangle - 0.1489\vert {}^1\psi_1,3\rangle + 0.0169\vert {}^1\psi_3,3\rangle$	0.0987	−0.0082
5	20.049	$-0.1576\vert 0,1\rangle + 0.6081\vert \mathrm{CT},1\rangle - 0.7612\vert {}^3\psi_1,1\rangle - 0.1606\vert {}^1\psi_1,1\rangle + 0.0103\vert {}^1\psi_2,1\rangle + 0.0084\vert {}^1\psi_3,1\rangle$	0.0205	0.0032
6	20.049	$-0.1576\vert 0,2\rangle + 0.6081\vert \mathrm{CT},2\rangle - 0.7612\vert {}^3\psi_1,2\rangle - 0.1606\vert {}^1\psi_1,2\rangle + 0.0103\vert {}^1\psi_2,2\rangle + 0.0084\vert {}^1\psi_3,2\rangle$	0.0205	0.0032
7	23.000	$1.0000\vert {}^3\psi_3,1\rangle$	0.0	0.0
8	23.000	$1.0000\vert {}^3\psi_3,2\rangle$	0.0	0.0
9	23.000	$1.0000\vert {}^3\psi_3,3\rangle$	0.0	0.0
10	24.200	$1.0000\vert {}^3\psi_2,1\rangle$	0.0	0.0
11	24.200	$1.0000\vert {}^3\psi_2,2\rangle$	0.0	0.0
12	24.200	$1.0000\vert {}^3\psi_2,3\rangle$	0.0	0.0
13	28.878	$-0.0901\vert 0,1\rangle + 0.5007\vert \mathrm{CT},1\rangle + 0.5561\vert {}^3\psi_1,1\rangle - 0.6388\vert {}^1\psi_1,1\rangle + 0.1197\vert {}^1\psi_2,1\rangle + 0.0977\vert {}^1\psi_3,1\rangle$	0.0200	0.0031
14	28.878	$-0.0901\vert 0,2\rangle + 0.5007\vert \mathrm{CT},2\rangle + 0.5561\vert {}^3\psi_1,2\rangle - 0.6388\vert {}^1\psi_1,2\rangle + 0.1197\vert {}^1\psi_2,2\rangle + 0.0977\vert {}^1\psi_3,2\rangle$	0.0200	0.0031
15	28.976	$0.5631\vert \mathrm{CT},3\rangle + 0.6126\vert {}^3\psi_1,3\rangle - 0.5024\vert {}^1\psi_1,3\rangle + 0.2350\vert {}^1\psi_3,3\rangle$	0.2467	−0.0908
16	31.000	$-0.6325\vert {}^1\psi_2,1\rangle + 0.7746\vert {}^1\psi_3,1\rangle$	0.2660	−0.1868
17	31.000	$-0.6325\vert {}^1\psi_2,2\rangle + 0.7746\vert {}^1\psi_3,2\rangle$	0.2660	−0.1868
18	31.000	$1.0000\vert {}^1\psi_2,3\rangle$	0.3325	−0.2335
19	31.654	$0.3228\vert \mathrm{CT},3\rangle + 0.2251\vert {}^3\psi_1,3\rangle + 0.2186\vert {}^1\psi_1,3\rangle - 0.8929\vert {}^1\psi_3,3\rangle$	0.1352	−0.1300
20	32.817	$-0.0728\vert 0,1\rangle + 0.4597\vert \mathrm{CT},1\rangle + 0.2772\vert {}^3\psi_1,1\rangle + 0.4383\vert {}^1\psi_1,1\rangle - 0.5556\vert {}^1\psi_2,1\rangle - 0.4536\vert {}^1\psi_3,1\rangle$	0.3950	0.0713
21	32.817	$-0.0728\vert 0,2\rangle + 0.4597\vert \mathrm{CT},2\rangle + 0.2772\vert {}^3\psi_1,2\rangle + 0.4383\vert {}^1\psi_1,2\rangle - 0.5556\vert {}^1\psi_2,2\rangle - 0.4536\vert {}^1\psi_3,2\rangle$	0.3950	0.0713
22	34.506	$0.0541\vert 0,1\rangle - 0.3593\vert \mathrm{CT},1\rangle - 0.1812\vert {}^3\psi_1,1\rangle - 0.6113\vert {}^1\psi_1,1\rangle - 0.5262\vert {}^1\psi_2,1\rangle - 0.4297\vert {}^1\psi_3,1\rangle$	1.0350	0.3822
23	34.506	$0.0541\vert 0,2\rangle - 0.3593\vert \mathrm{CT},2\rangle - 0.1812\vert {}^3\psi_1,2\rangle - 0.6113\vert {}^1\psi_1,2\rangle - 0.5262\vert {}^1\psi_2,2\rangle - 0.4297\vert {}^1\psi_3,2\rangle$	1.0350	0.3822
24	35.035	$-0.3774\vert \mathrm{CT},3\rangle - 0.1810\vert {}^3\psi_1,3\rangle - 0.8232\vert {}^1\psi_1,3\rangle - 0.3836\vert {}^1\psi_3,3\rangle$	0.0028	0.0039

[a] See Figure 5.

absorption intensity of the lowest excited singlet. The exciton coupling interaction between the lowest (π,π^*) excited singlets, K_{AB}, was evaluated as 500 cm^{-1} from the dipole–dipole interaction of the observed transition dipoles. The one-electron terms X and Y, which yield a charge migration between metal d_π and ligand-oxygen p_π orbitals, are set commonly to 3×10^3 cm^{-1} because the absolute values of orbital coefficients on oxygens of the ligand LUMO and HOMO are almost identical. An analogous value was obtained by the semiempirical molecular orbital calculations.[36]

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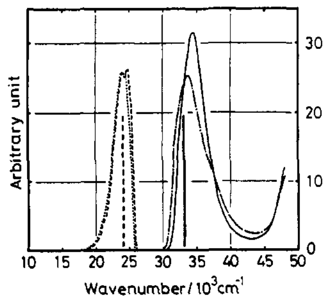

Figure 4. Absorption spectra of [$Sc(acac)_3$] (–·–), [$Y(acac)_3$] (—) in methanol and phosphorescence spectra of [$Sc(acac)_3$] (···), [$Y(acac)_3$] (- - -) in ethanol/methanol (1:1) glass at 77 K. The excitation energies of the ligand (π,π^*) excited triplet (- - -) and singlet (—) used for calculation are shown by the vertical lines.

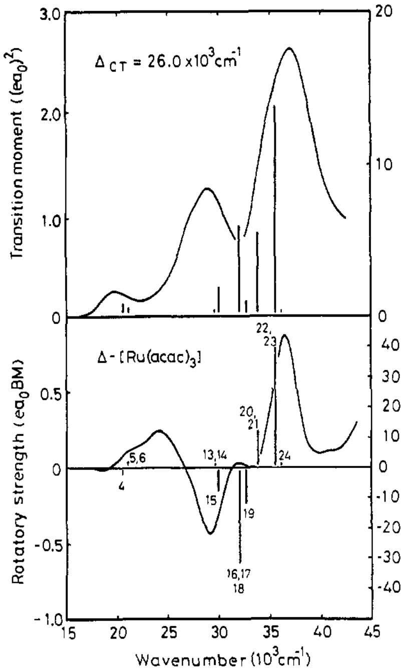

Figure 5. Calculated absorption and CD spectra of Δ-[$Ru(acac)_3$]. The assignments are presented by giving the numbering of the excited states defined in Table III.

On the same basis, the exchange integrals K and K' are set equally as 600 cm^{-1}.

Diagonalization of the configuration interactions not only yields admixtures of the excited configurations but also splits the ground-state sublevels as summarized in Table III. The interactions of the LMCT excited states stabilized the ground-state degenerate sublevels $|0,1\rangle$ and $|0,2\rangle$. A gap between $|0,1\rangle$, $|0,2\rangle$ and $|0,3\rangle$ is greater than 1000 cm^{-1}, and thus the complex should be in the lowest ground-state sublevels. With the parameters used for reproduction of spectrum of [$Ru(acac)_3$] as well as the empirical spin–orbit coupling constant ζ = 1000 cm^{-1},[37,38] theory yields g values ($g_\parallel$ = 1.45, $g_\perp$ = 2.30) compatible with those obtained by ESR measurements ($g_\parallel$ = 1.45, $g_\perp$ = 2.45, 2.16).[39] The observed paramagnetic shifts of NMR signals are mainly attributable to the Fermi contact term, which is ascribed to the delocalization of the unpaired electron over the ligands; however, it is noted that the sign of the shift is consistent with $|g_\parallel|$ = 1.45 and $|g_\perp|$ = 2.30 rather than $|g_\parallel|$ = 2.30 and $|g_\perp|$ = 1.45. This also suggests the degenerate ground state.

Figure 5 shows the calculated absorption and CD spectra of the Δ isomer. The observed absorption spectrum is reproduced with Δ_{CT} = 26 000 cm^{-1}. A remarkable reduction of the intensity of the ligand (π,π^*) band arises from the greater splitting in the ground-state sublevels of low spin [$Ru(acac)_3$] in contrast with the small zero-field splitting in high-spin [$Fe(acac)_3$] but not from granting the intensity to the forbidden $^3(\pi,\pi^*)$ transitions and the LMCT transition by the configuration-interaction admixing. In fact, no reduction of the intensity is observed in [$Fe(acac)_3$].

In the present work, the contributions of spin–orbit coupling to the low-energy excited states are completely ignored. However, theory correctly predicts the CD spectrum of Δ-[$Ru(acac)_3$] as observed with the isomer in the earlier eluted fraction.

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Registry No. [$Ru(acac)_3$], 14284-93-6; Δ-[$Ru(acac)_3$], 31378-27-5; Λ-[$Ru(acac)_3$], 31378-26-4; [$Ru(dpm)_3$], 38625-54-6; [$Ru(hfac)_3$], 16827-63-7; [$Fe(acac)_3$], 14024-18-1; [$Sc(acac)_3$], 14284-94-7; [$Y(acac)_3$], 15554-47-9; cellulose tris(phenylcarbamate), 9047-07-8.

Supplementary Material Available: Plots of the NMR data (Figure A1) and a listing of the transition moments over the substates (Table A1) (2 pages). Ordering information is given on any current masthead page.

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