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Article

Effects of Central Metal Ions on Vibrational Circular Dichroism Spectra of Tris-(β-diketonato)metal(III) Complexes

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Vibrational circular dichroism (VCD) spectra of a series of [M(III)(acac)$_3$] (acac = acetylacetonato; M = Cr, Co, Ru, Rh, Ir, and Al) and [M(III)(acac)$_2$(dbm)] (dbm = dibenzoylmethanato; M = Cr, Co, and Ru) have been investigated experimentally and/or theoretically in order to see the effect of the central metal ion on the vibrational dynamics of ligands. The optical antipodes give the mirror-imaged spectra in the region of 1700–1000 cm^{-1}. The remarkable effect of the central metal ion is observed experimentally on the VCD peaks due to C–O stretches (1500–1300 cm^{-1}) for both [M(III)(acac)$_3$] and [M(III)(acac)$_2$(dbm)]. In the case of Δ-[M(III)(acac)$_3$], for example, the order of frequency of two C–O stretches (E and A$_2$ symmetries) is dependent on the kind of a central metal ion as follows: E (–) > A$_2$ (+) for M = Co, Rh, and Ir, while A$_2$ (+) > E (–) for M = Cr and Ru. In the case of Δ-[M(III)(acac)$_2$(dbm)], the order of frequency of three C–O stretches (A, B, and B symmetries) is as follows: A (–) > B (+) > B (+) for Co(III), B (+) > A (-) > B (-) for Cr(III), and A (-) > B (+) > B (–) for Ru(III). These results imply that the energy levels of C–O stretches are delicately affected by the kind of central metal ion. Since such detailed information is not obtained from the IR spectra alone, the VCD spectrum can probe the effect of the central metal ion on interligand cooperative vibration modes.

Introduction

Chirality of metal complexes has been attracting continuing interest in the fundamental area of coordination chemistry.[1] In the practical area, chiral octahedral metal complexes are employed extensively as catalysts, sensors, and chiral source of induction of helix and so on.[2–8] Their functions as a chiral source are manifested through the discrimination of molecular chirality, the transfer of chirality from one species to another, and the amplification of chirality to a supramolecular scale. A key to useful application of chiral metal complexes lies in understanding the cooperative effects of the dynamical motions among vicinal ligands and the degree of participation of the central metal ion in the effects. Knowledge of this kind has been obtained by various

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spectroscopic methods such as electronic circular dichroism (ECD),[9] NMR,[10,11] and photophysical measurements.[12]

Vibrational circular dichroism (VCD) is the extension of electronic circular dichroism (ECD) into the infrared and near-infrared regions of the spectrum where vibrational transitions occur in the ground electronic state of a molecule.[13−19] The method measures the differential absorption of left versus right circularly polarized IR radiation by a molecular vibration transition.[13] The advantage of VCD over ECD is the large amount of information for $3N - 6$ vibrations, where N is the number of atoms in the molecule.[13−16] Accordingly VCD has become one of the powerful tools for understanding the stereochemical details of chiral molecules.[13−44] In particular, when the VCD method is applied to chiral metal complexes,[24−31,42−44] it is hoped that the method reveals dynamical aspects of the cooperative motions of ligands and central metal ions that are unfeasible by other spectroscopic means. For example, pioneering works by Nafie and co-workers[27] revealed the presence of a ring current extending ligands and a central metal ion for bis(acetylacetonato)(L-alaninato)cobalt (III) complexes. Moreover, the coupled oscillator mechanism is confirmed by analyzing the VCD spectra in the mid-infrared region for C−C stretches.

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Motivated by these works, the present work has studied the VCD spectra of a series of tris(acetylacetonato)metal(III) and bis(acetylacetonato)(dibenzoylmethanato)metal(III). The reason for choosing these molecules is that the infrared spectra of tris(acetylacetonato)metal(III) complexes have been thoroughly investigated theoretically.[45−47] The main intense bands are successfully assigned in conjunction with density functional theory (DFT) calculations. According to our preliminary VCD measurements of chiral tris(acetylacetonato)metal(III) complexes,[43] it has been found that the order of energy levels is opposite, for example, for the stretching vibrations of C−O bonds (A_2 and E symmetries) between Co(III) and Cr(III) complexes. These results suggest the significant effects of the d-electron configuration of a central metal ion on vibration transitions. For examining the validity of observed effects of the central metal ion for wider classes of metal complexes, this work attempted a systematic VCD study on two kinds of tris-chelated complexes with a series of different metal ions. As a result, it has been revealed that the configuration of d-electrons in a central metal ion has a dramatic effect on the VCD spectral shapes. With the help of theoretical calculations, it has been concluded that the modes representing the interligand correlative vibrations of C−O stretches are most significantly affected by the type of central metal ion.

Results

VCD Spectra of [M(III)(acac)$_3$]. Figure 1 panels a−e show the observed VCD (upper) and IR (lower) spectra for [M(III)(acac)$_3$] with M = Co, Rh, Ir, Cr, and Ru in $CDCl_3$, respectively. All five complexes give similar IR spectra in the whole spectral range (1700−1000 cm^{-1}). Main intense bands were assigned previously in detail in the case of M = Co and Cr.[45] Both complexes are reported to undergo no Jahn−Teller distortion. In the IR spectra, the intense band around 1570 cm^{-1} is assigned mainly to C−O stretches. The intense band around 1520 cm^{-1} is assigned mainly to C−C stretches. The band around 1430 cm^{-1} involves multiple vibrations arising from CH_3 bending bands. The intense band around 1380 cm^{-1} is mainly assigned to C−O stretches.[45] For the Ru(III) complex alone, a small shoulder observed at 1340 cm^{-1} is assigned to C−O stretching.

In VCD measurements, the antipodes give mirror-imaged spectra for all investigated cases. When the spectra are compared among the complexes, there is no remarkable difference in the range of 1700−1500 cm^{-1}, which corresponds to the C−C and C−O stretching vibrations. The band around 1520 cm^{-1}, which is mainly assigned to the C−C stretching, exhibits a positive−negative bisignate shape from higher to lower frequency for the Δ isomers or vice versa for the Λ isomers. Previously the splitting of the band was interpreted in terms of the coupled oscillator mechanism between vicinal ligands.[27] For the Ru(III) complex alone, the appreciable broadening of a peak is observed in this frequency region.

The situations are contrasted with the bands due to C−O stretches at 1500−1300 cm^{-1}. Notably, the positions of the positive and negative peaks are dependent on the type of metal ion. In the case of Co(III), Rh(III), and Ir (III) (denoted by group 1), the Δ enantiomer exhibits negative and positive peaks from higher to lower frequency. As expected, the Λ enantiomer of the same complex exhibits the opposite feature. To the contrary, in the case of Cr(III) and Ru(III) (denoted by group 2), the Δ enantiomer exhibits positive and negative peaks from higher to lower frequency. In other words, the bisignate nature of the peak is opposite in complexes of groups 1 and 2. In the case of [Ru(III)(acac)$_3$], the separation between the coupled peaks is so large (ca. 40 cm^{-1}) that the peak at lower frequency arises from the shoulder at 1341 cm^{-1} in the IR spectra. As an additional feature, in the case of the Ru(III) complex, the broad peak is observed at 1300−1100 cm^{-1}, which is ascribed to the participation of the d−d transition in this region.[29] Table 1 summarizes the experimental VCD of C−O stretching in Δ-[M(III)(acac)$_3$].

The calculated IR and VCD spectra of the Δ enantiomers of [M(III)(acac)$_3$] with M = Co, Rh, Ir, Cr, and Ru) are shown in Figure 2 panels a−e, respectively. The calculation of IR spectra well reproduces the observed spectra except for the shift of each peak position toward higher frequency (ca. 70 cm^{-1}). In previously reported calculations at the same level [DFT(B3LYP/6-31G(d)], the correct frequency was obtained by introducing a scale factor of 0.92 for C−O stretching.[45]

The calculated VCD spectra in the range of 1700−1500 cm^{-1} are nearly identical among the investigated five complexes. A calculated bisignate band around 1580 cm^{-1}, assigned to C−C stretches, corresponds to the bisignate band around 1520 cm^{-1} in the observed spectra. The single peak around 1630 cm^{-1}, which is assigned to one of the doubly degenerate E modes of C−O stretching, corresponds to the peak around 1570 cm^{-1} in the observed spectra. Thus it is confirmed both experimentally and theoretically that the electronic properties of the central metal ion little affect the spectral features of these bands.

It is interesting to see how the theory predicts the effect of a central metal ion on the bisignate bands observed at 1500−1300 cm^{-1} due to C−O stretches. In the case of Δ-[Co(III)(acac)$_3$], the calculated peaks consist of negative (doubly degenerate E) and positive (A_2) composites at 1473 and 1468 cm^{-1}, respectively. These two peaks correspond to the negative and positive ones at 1396 and 1381 cm^{-1} in the experimental spectra, respectively. Moreover, the calculation predicts correctly the lower intensity of the negative peak than that of the positive one. The same features are predicted for Δ-[Rh(III)(acac)$_3$] and Δ-[Ir(III)(acac)$_3$], confirming the agreement between the observed and calculated spectra.

In the case of Δ-[Cr(III)(acac)$_3$], the calculated peaks are composed of positive (A_2) and negative (doubly degenerate E) peaks at 1464 and 1461 cm^{-1}, respectively. These two peaks correspond to the positive and negative ones at 1391

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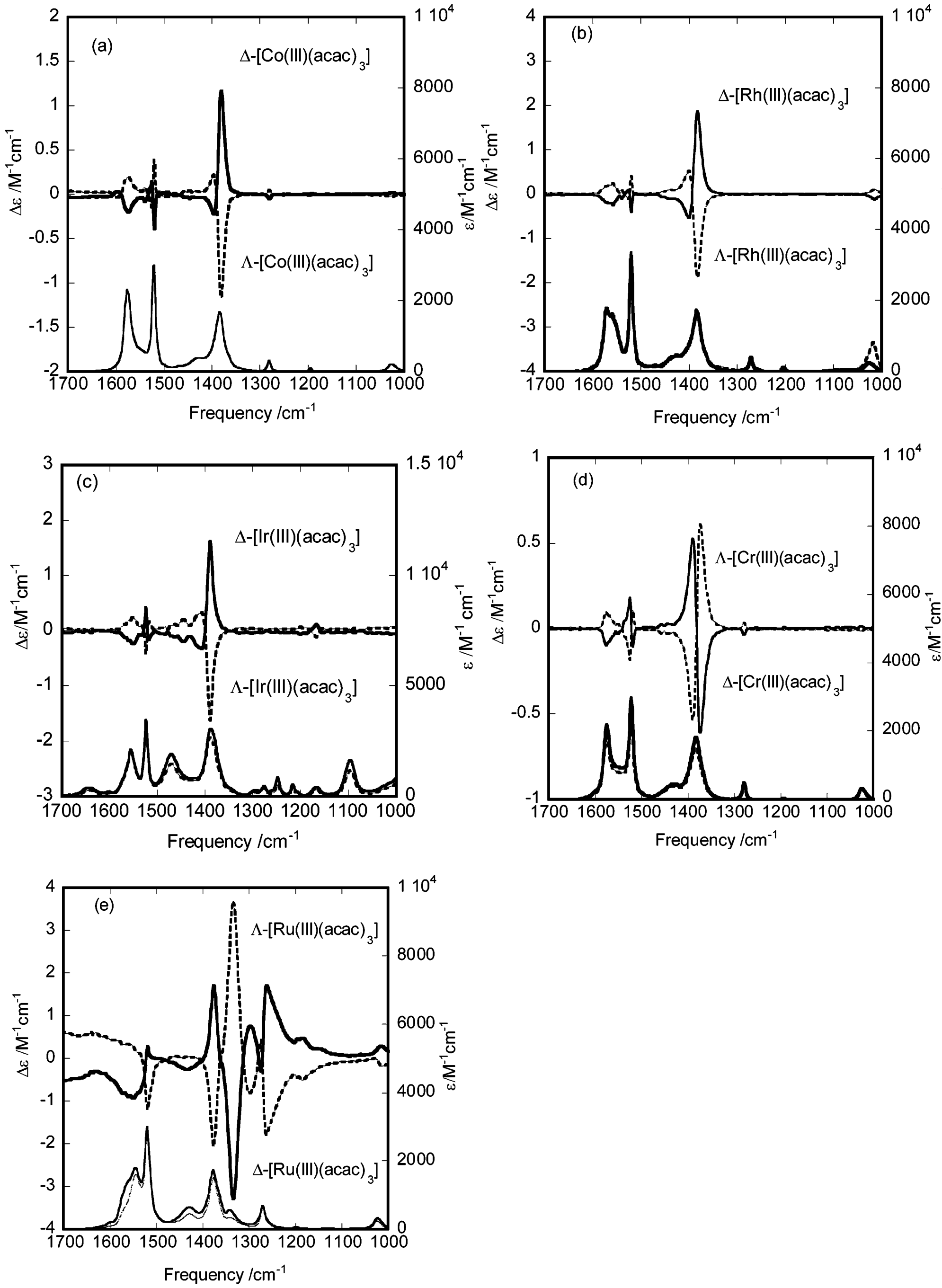

Figure 1. Observed IR (lower) and VCD (upper) spectra of [M(III)(acac)$_3$] [where M = (a) Co, (b) Rh, (c) Ir, (d) Cr, and (e) Ru] in CDCl$_3$. Solid and dotted curves correspond to Δ- and Λ-enantiomers, respectively.

Table 1. Observed Main C−O Vibrations in VCD Spectra of Δ-[M(III)(acac)$_3$]

frequency, cm^{-1}				
Δ-[Co(III) (acac)$_3$]	Δ-[Rh(III) (acac)$_3$]	Δ-[Ir(III) (acac)$_3$]	Δ-[Cr(III) (acac)$_3$]	Δ-[Ru(III) (acac)$_3$]
1381 (+)	1383 (+)	1389 (+)	1374 (−)	1298 (+)
1396 (−)	1401 (−)	1407 (−)	1391 (+)	1335 (−)
				1377 (+)
1575 (−)	1567 (−)	1551 (−)	1576 (−)	1561 (−) broad

and 1374 cm^{-1} in the experimental spectra, respectively. The calculation also predicts correctly that these peaks show nearly the same intensity. In the case of [Ru(III)(acac)$_3$], calculation is performed with the assumption that the molecule has C_2 symmetry. The assignment of each vibration mode is performed, however, under the approximation of D_3 symmetry. The theory predicts positive (A_2) and negative (E) peaks at 1457 and 1402 cm^{-1} for [Ru(III)(acac)$_3$], respectively. The negative peak is located at a position remote from the positive one, so that it corresponds to the small peak at 1402 cm^{-1} near the large peak in the IR spectrum. These features roughly agree with the experimental observations. The results have confirmed the validity of the present magnetic field perturbation (MFP) theory in the case of open-shell systems. To summarize the above results, the effect of metal ions on the bisignate band of C−O stretches at 1500−1300 cm^{-1} is rationalized in terms of the difference in the

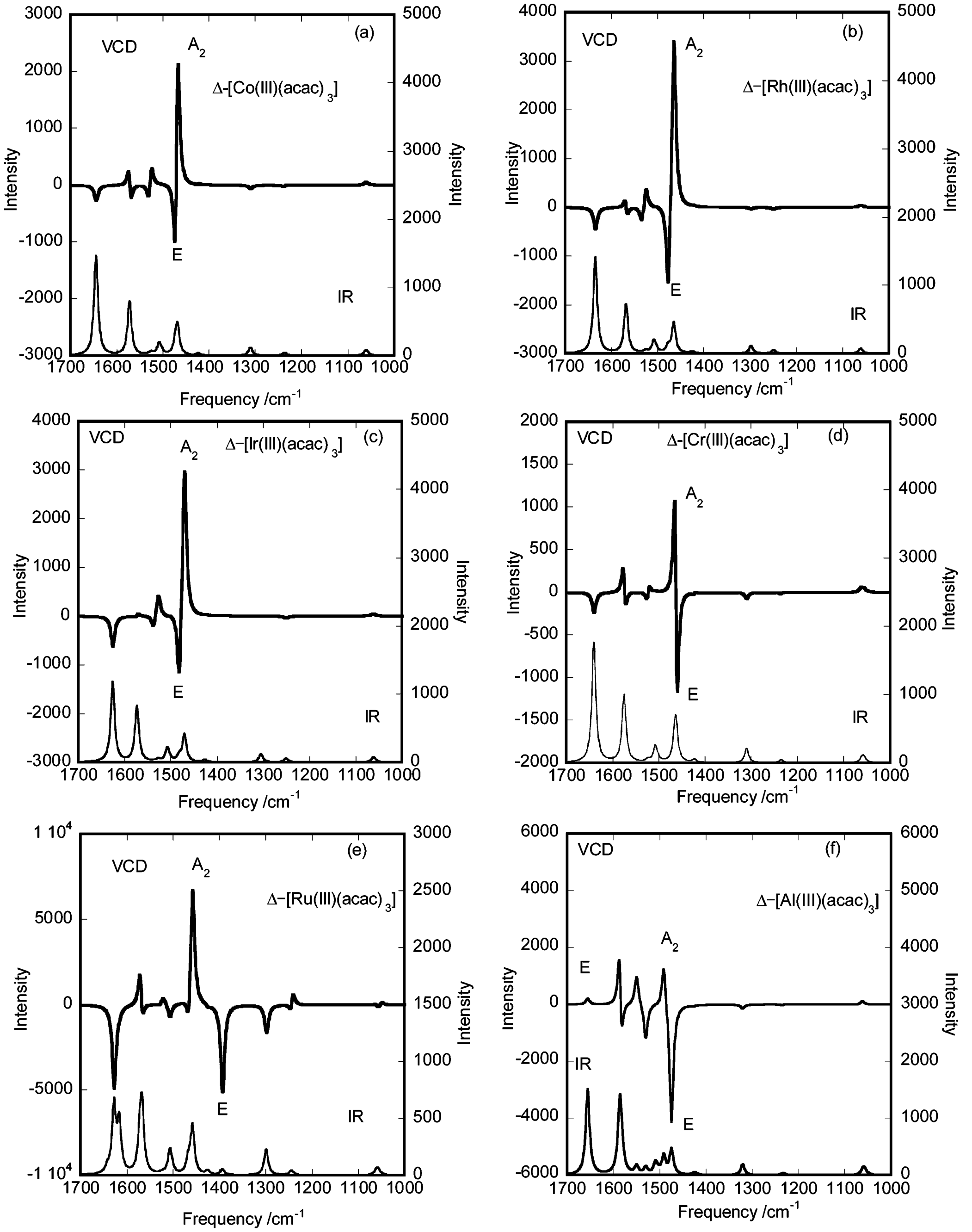

Figure 2. Calculated IR (lower) and VCD (upper) spectra of Δ-[M(III)(acac)$_3$] [where M = (a) Co, (b) Rh, (c) Ir, (d) Cr, (e) Ru, and (f) Al]. Although [Ru(III)(acac)$_3$] is calculated for C_2 symmetry, the assignment is done under the approximation of D_3 symmetry. The other five complexes are assumed to belong to D_3 symmetry. No correction is made by introducing a scale factor for these spectra.[28,45]

frequency order of two composite peaks (A_2 and E). The only aspect that the theory fails in predicting is the broad peak at 1300−1100 cm^{-1} in the case of the Ru(III) complex.

[Al(III)(acac)$_3$] with no d-electron was calculated as shown in Figure 2f. In the case of Δ-[Al(III)(acac)$_3$], the calculated peaks are composed of positive (A_2) and negative (doubly degenerate E) peaks at 1492 and 1475 cm^{-1}, respectively. The single positive peak at 1656 cm^{-1}, which is one of the doubly degenerate E modes, is assigned as C−O stretching. More detailed results on the experimental and calculated frequencies of [M(III)(acac)$_3$] are presented in the Supporting Information. The assignment of each peak has been done according to the calculated results.

VCD Spectra of [M(III)(acac)$_2$(dbm)]. Figure 3 panels a−c show, respectively, the electronic circular dichroism (ECD) spectra of methanol solutions of enantiomeric [M(III)(acac)$_2$(dbm)] (M = Co, Cr, and Ru) (Chart 1b). The absolute configuration of these complexes is determined as indicated in the figures by comparing the observed spectra with those of corresponding [M(III)(acac)$_3$] in the d−d transition region (400−600 nm).[49]

Figure 4 panels a−c show the observed IR (lower) and VCD (upper) spectra of the CDCl$_3$ solutions of [M(III)(acac)$_2$(dbm)] (M = Co, Cr, and Ru), respectively. [M(III)-

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(48) Okamoto, Y.; Yashima, E.; Hatada, K. *J. Chem. Soc., Chem. Commun.* **1984**, 1051.

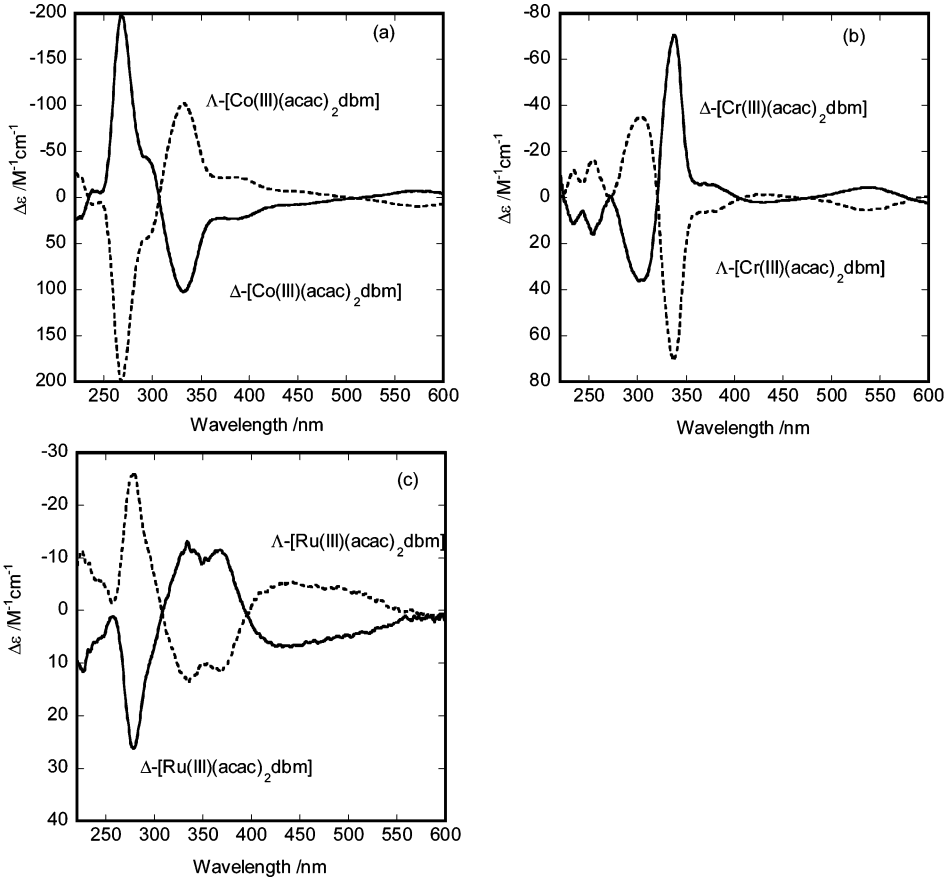
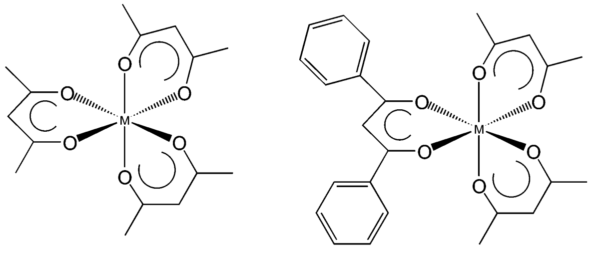


Figure 3. ECD spectra of [M(III)(acac)$_2$(dbm)] [where M = (a) Co, (b) Cr, and (c) Ru] in methanol. Solid and dotted curves correspond to Δ- and Λ-enantiomers, respectively.

Chart 1. Structures of (a) Δ-[M(III)(acac)$_3$] and (b) Δ-[M(III)(acac)$_2$(dbm)]



(a) Δ-[M(III) (acac)$_3$]

(b) Δ-[M(III) (acac)$_2$(dbm)]

(acac)$_2$(dbm)] displays C_2 symmetry. The IR spectra of [Co(III)(acac)$_2$(dbm)] and [Cr(III)(acac)$_2$(dbm)] are nearly identical in the entire range of 1700−1000 cm^{-1}. Compared with the IR spectra of the corresponding tris-chelated complexes, the additional peak appears around 1480 cm^{-1}. This is assigned to the C−H ring stretching of a dbm ligand. Another additional peak at 1543 cm^{-1} is assigned to the combination of C−O and C−C stretches of a dbm ligand. The combination of C−O and C−C stretches of a dbm ligand is observed at 1580 cm^{-1}. The IR spectrum of [Ru(III)(acac)$_2$(dbm)] is similar to those of [Co(III)(acac)$_2$(dbm)] and [Cr(III)(acac)$_2$(dbm)] in the same range except for the overlapping of composite peaks in the range of 1600−1500 cm^{-1} due to slight broadening.

In the VCD spectra of [M(III)(acac)$_2$(dbm)], peaks are low and not definite in the 1700−1500 cm^{-1} range due to the low signal-to-noise ratio. In the case of [Cr(III)(acac)$_2$(dbm)], the small peaks around 1580 and 1520 cm^{-1} are assigned to C−O and C−C stretches, respectively. These peaks show the same signs for the same enantiomers of the investigated three complexes. The remarkable effect of the central metal ion is observed in the main peaks at 1500−1300 cm^{-1} arising from C−O stretches. In the case of Δ-[Co(III)(acac)$_2$(dbm)], the intense band at 1380 cm^{-1} in its IR spectrum is split into two with one negative peak at 1396 cm^{-1} and one positive peak at 1377 cm^{-1}. To the contrary, in the case of Δ-[Cr(III)(acac)$_2$(dbm)], the corresponding strong peak at 1380 cm^{-1} in the IR spectrum is split into two with one positive peak at 1389 cm^{-1}and one negative peak at 1373 cm^{-1}. In the case of Δ-[Ru(III)(acac)$_2$(dbm)], the bisignate feature at 1500−1300 cm^{-1} is identical with that of Δ-[Cr(III)(acac)$_2$(dbm)], or the positive peak at 1373 cm^{-1} and the negative peak at 1334 cm^{-1}. The positive peak is thought to originate from the strong peak at 1373 cm^{-1} in the IR spectrum, while the negative peak is so distant from that peak that it originates from the weak broad band around 1340 cm^{-1}. As was already seen for [Ru(III)(acac)$_3$], the broad band exists at 1300−1100 cm^{-1}. Table 2 summarizes the main C−O peaks in the VCD observed spectra of Δ-[M(III)(acac)$_2$(dbm)].

Detailed assignment of the above peaks can be done with the help of the calculated VCD spectra. Figure 5 panels a−c

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(49) Drake, A. F.; Gould, J. M.; Mason, S. F.; Rosin, C.; Woodley, F. J. *Polyhedron* **1983**, *2*, 537.

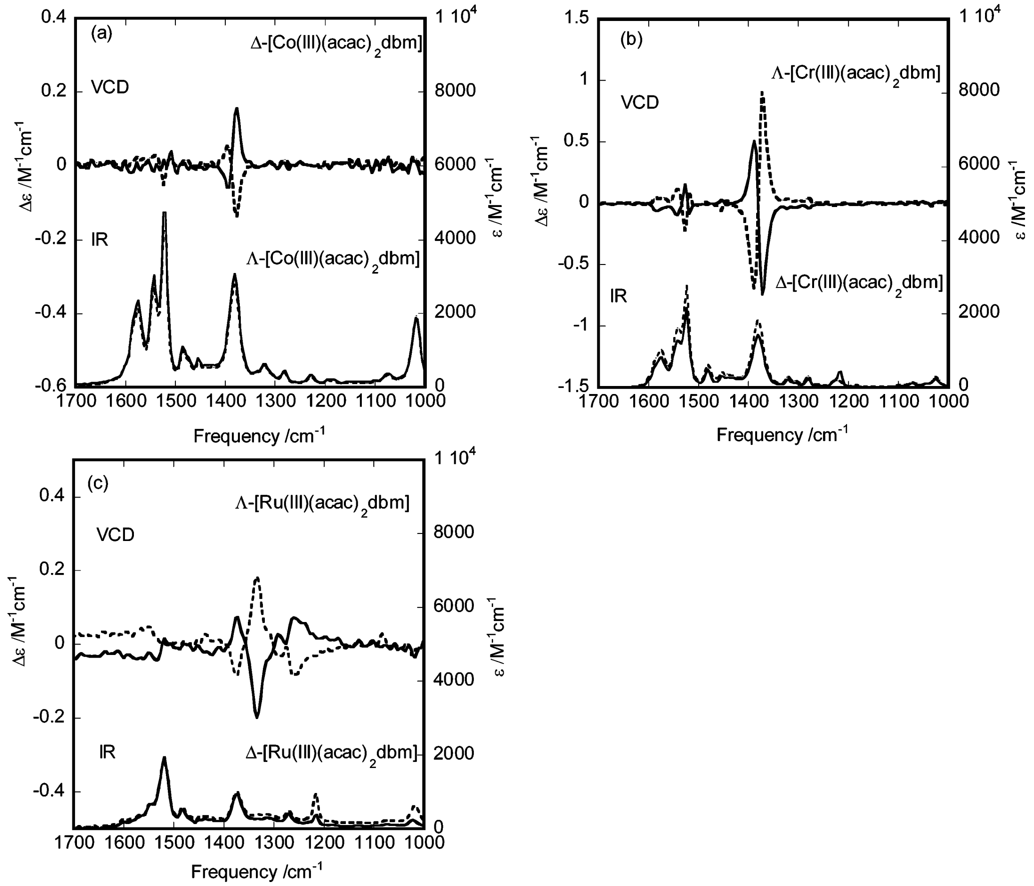


Figure 4. Observed spectra of [M(III)(acac)$_2$(dbm)] [where M = (a) Co, (b) Cr, and (c) Ru] in CDCl$_3$. Solid and dotted curves correspond to Δ- and Λ-enantiomers, respectively.

Table 2. Observed Main C−O Vibrations in VCD Spectra of Δ-[M(III)(acac)$_2$(dbm)]

frequency, cm^{-1}		
Δ-[Co(III)(acac)$_2$(dbm)]	Δ-[Cr(III)(acac)$_2$(dbm)]	Δ-[Ru(III)(acac)$_2$(dbm)]
1354 (+) small	1323 (−)	1296 (+) weak
1377 (+)	1373 (−)	1334 (−)
1396 (−)	1389 (+)	1373 (+)
	1585 (−)	1546 (−) weak

show the calculated IR (upper) and VCD (lower) spectra of Δ-[M(III)(acac)$_2$(dbm)] (M = Co, Cr, and Ru), respectively. The complexes are assumed to have C_2 symmetry. No correction is made by use of any scale factor. The calculated IR spectra reproduce the experimental IR spectra in the whole wavenumber region except for the shift of the peak positions toward higher frequency.

The bisignate features observed around 1370−1390 cm^{-1} due to C−O stretches are interpreted as follows. In the case of Δ-[Co(III)(acac)$_2$(dbm)], the negative A-mode peak at 1473 cm^{-1}, the positive B-mode peak at 1471 cm^{-1}, and the additional positive B-mode peak at 1463 cm^{-1} correspond to the negative peak at 1396 cm^{-1}, the positive peak at 1377 cm^{-1}, and the small shoulder around 1354 cm^{-1} in the observed spectrum, respectively. In the calculated spectra, the negative peak predicted at 1607 cm^{-1} is assigned to C−O stretch (A-mode), in which a dbm ligand is out of phase with the other acac ligands in-phase. This peak is not confirmed to exist in the observed spectra because of the low signal-to-noise ratio at 1700−1500 cm^{-1}.

In the case of Δ-[Cr(III)(acac)$_2$(dbm)], the positive B-mode peak at 1463 cm^{-1}, the negative A-mode peak at 1461 cm^{-1}, and the negative B-mode peak at 1451 cm^{-1} in the calculated spectrum correspond to the positive peak at 1389 cm^{-1}, the negative peak at 1373 cm^{-1}, and the small shoulder around 1323 cm^{-1} in the observed spectrum, respectively. The single negative peak that is assigned to C−O stretch (A-mode) is predicted at 1602 cm^{-1}. This corresponds to the small negative peak at 1543 cm^{-1} in the observed spectrum.

In the case of Δ-[Ru(III)(acac)$_2$(dbm)], the positive B-mode peak at 1452 cm^{-1} , the negative B-mode peak at 1397 cm^{-1}, and the additional small negative A-mode peak predicted at 1465 cm^{-1} in the calculated spectrum correspond to the positive peak at 1373 cm^{-1} and the negative peak at 1334 cm^{-1} in the observed spectrum, respectively. The large separation between the positive and negative peaks in the bisignate nature for this complex is predicted theoretically. The single negative peak at 1626 cm^{-1} is assigned to C−O stretch (B-mode), in which two acac ligands stretch out of phase with a dbm ligand frozen. This corresponds to the broad band at 1700−1500 cm^{-1} in the observed spectrum. Detailed results on the observed and calculated spectra of [M(III)(acac)$_2$(dbm)] are presented in the Supporting Information.

Discussion

The IR spectra of a series of tris(acetylacetonato)metal(III) complexes were previously investigated in detail by both

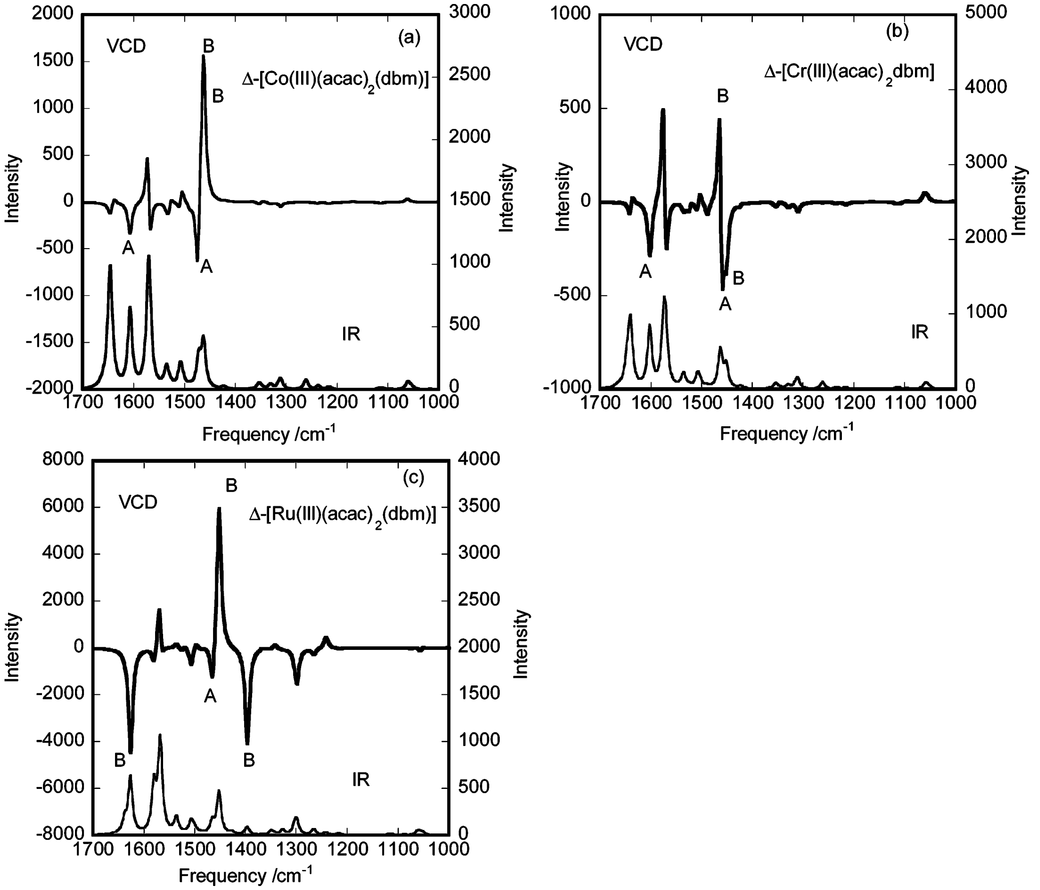


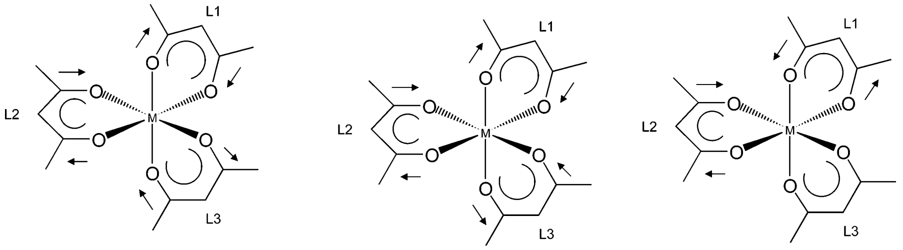
Figure 5. Calculated IR (lower) and VCD (upper) spectra of Δ-[M(III)(acac)$_2$(dbm)] [where M = (a) Co, (b) Cr, and (c) Ru]. No correction is made by introducing a scale factor for these spectra.[28,45]

experiments and ab initio calculation.[45,46] The effects of central metal ions on VCD spectra have been reported previously in several examples.[24−26,29,42,43] A complex with a metal ion of open shell, for example, gives higher intensity than one with a metal ion of closed shell. The facts are rationalized in terms of the presence of low-lying excited electronic states.[29]

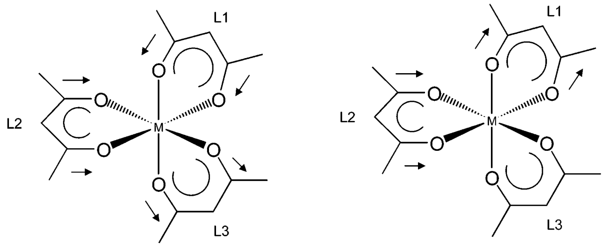
For the present tris(β-diketonato)metal(III) complexes, some of the VCD peaks are indifferent to the type of central metal ion, while others are dependent on the central metal ion in both intensity and location. The former category includes the C−C stretches around 1520 cm^{-1} and the C−O stretches at 1700−1500 cm^{-1}. As for the C−C stretches, the concerned bonds are so remote from a central metal ion that the vibrations are not influenced by its electronic configuration. As for the C−O stretches, Schemes 1 and 2 show the representative modes of C−O stretches cooperative among the coordinated ligands for [M(III)(acac)$_3$] and [M(III)(acac)$_2$(dbm)], respectively. The above C−O stretch at 1700−1500 cm^{-1} corresponds to the modes in Schemes 1d,e and 2d,e for [M(III)(acac)$_3$] and [M(III)(acac)$_2$(dbm)], respectively. Since these two modes (d and e) are completely degenerate, an isolated single peak appears in both IR and VCD spectra. Under such situations, the difference of the central metal ion has little effect on the spectral features of peak intensity and position. Thus the signs of these bands in this region can be a diagnosis of the ΔΛ configuration of these complexes.

In contrast to the above vibrations, the VCD spectra in the region of C−O stretches (1500−1300 cm^{-1}) of [M(III)(acac)$_3$] are dramatically dependent on the type of central metal ion as shown in Figure 1. With the help of the theoretical analyses, the influence of a central metal ion in this region is successfully interpreted in terms of the difference in the frequency order of two composites (A_2 and E) of the interligand correlative vibrations. The investigated five [M(III)(acac)$_3$] complexes are classified into two groups: the frequency of the C−O stretch with E symmetry is higher than that of the C−O stretch with A_2 symmetry in the case of M = Co $(e_g)^6$, Rh $(e_g)^6$, and Ir $(e_g)^6$ (denoted by group 1), while the situations are reversed in the case of M = Cr $(e_g)^3$ and Ru $(e_g)^5$ (denoted by group 2). Since the A_2- and E-mode vibrations represent the in-phase and out-of-phase stretches of three ligands, respectively, as schematically shown in Scheme 1a−c, the above results imply that the energy of such an interligand correlative vibration depends on the d-electron configuration of a central metal ion in a symmetry-dependent way. For [Ru(III)(acac)$_3$], broad bands are observed around 1200 cm^{-1}. This feature indicates the presence of low-lying excited electronic states of 5d electrons. A similar effect is not observed for [Rh(III)(acac)$_3$] and [Ir(III)(acac)$_3$], because such states are absent for the complex of a metal ion with a closed shell. Table 3 summarizes the calculated C−O stretches at 1500−1300 cm^{-1} of [M(III)(acac)$_3$]. The calculated VCD spectrum of Δ-[Al(III)(acac)$_3$] [Al(III) $(e_g)^0$] shows that the complex

Scheme 1. Schematic Drawings of A_2- and E-Modes in the C−O Vibrations of Δ-[M(III)(acac)$_3$][a]



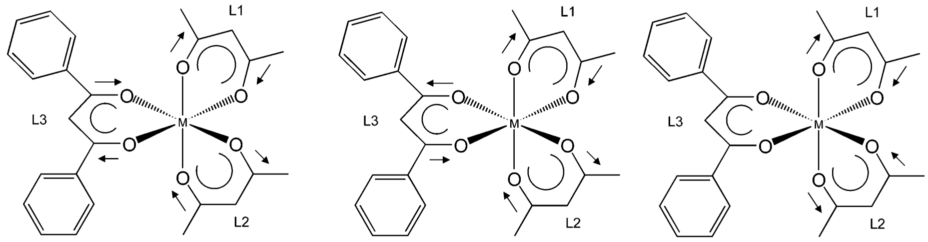
(a) A_2-mode **(b) E-mode** **(c) E-mode**



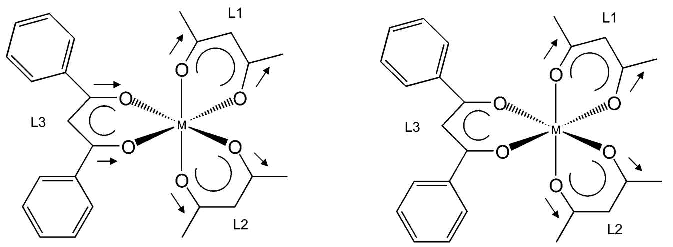
(d) E-mode **(e) E-mode**

[a] (a) A_2-mode: L1, L2, and L3 are all in-phase. (b) E-mode: L1 and L2 are in-phase, while L3 is out-of-phase. (c) E-mode: L3 is frozen, while L1 and L2 are out-of-phase. (d) E-mode: L1 and L2 are in-phase, while L3 is out-of-phase. (e) E-mode: L1 and L2 are out-of-phase. E-mode (b, c) and E-mode (d, e) are degenerate.

Scheme 2. Schematic Drawings of A- and B-Modes in the C−O Vibrations of Δ-[M(III)(acac)$_2$(dbm)][a]



(a) B-mode **(b) B-mode** **(c) A-mode**



(d) A-mode **(e) B-mode**

[a] (a) B-mode: L1, L2, and L3 (dbm) are all in-phase. (b) B-mode: L1 and L2 are in-phase, while L3 is out-of-phase. (c) A-mode: L1 and L2 are out-of-phase. (d) A-mode: L1 and L2 are in-phase, while L3 is out-of-phase. (e) B-mode: L1 and L2 are out-of-phase.

belongs to group 2. Optical resolution of [Al(III)(acac)$_3$] is reported to be performed at as low as −80 °C.[48] Thus the VCD measurement of this substitution-labile complex remains a challenging work. At present, there is no simple rule to relate the above classification of VCD features (groups 1 and 2) with the d-electron configuration of a central metal ion.

A similar effect of a central metal ion on the VCD spectrum in the C−O stretches (1500−1300 cm^{-1}) is observed for [M(III)(acac)$_2$(dbm)]. The symmetry of a complex is lowered from D_3 to C_2. Theoretically, the band due to C−O stretches in this region is a composite of three vibrational modes (A, B, and B) representing the correlative vibrations among three ligands (Scheme 2a−c). In the A-mode, the C−O bonds of two acetylacetonato ligands stretch out-of-phase with no stretch of C−O bonds of dbm. In one of the B-modes, all of the C−O bonds stretch in-phase. In another B-mode, two acac ligands stretch in-phase. By comparing the observed and calculated VCD spectra, the following orders are deduced as to the frequencies of these three modes: A (−) > B (+) > B (+) for Δ-[Co(III)(acac)$_2$-(dbm)], B (+) > A (−) > B (−) for Δ-[Cr(III)(acac)$_2$(dbm)],

Table 3. Calculated Effects of the Central Metal Ion of [M(III)(acac)$_3$] on VCD Spectra of C−O Vibrations

complex with D_3 symmetry	config	sign of split peaks of C−O stretching, assignment: higher frequency	sign of split peaks of C−O stretching, assignment: lower frequency	order of vibration modes in frequency[a]
Δ-[Co(III)(acac)$_3$]	d^6	(−) at 1473 cm^{-1} degenerate E-mode[b]	(+) at 1468 cm^{-1} A$_2$-mode[c]	A$_2$ (ip) < E (oop)
Δ-[Rh(III)(acac)$_3$]	d^6	(−) at 1477 cm^{-1} degenerate E-mode[b]	(+) at 1465 cm^{-1} A$_2$-mode[c]	A$_2$ (ip) < E (oop)
Δ-[Ir(III)(acac)$_3$]	d^6	(−) at 1482 cm^{-1} degenerate E-mode[b]	(+) at 1471 cm^{-1} A$_2$-mode[c]	A$_2$ (ip) < E (oop)
Δ-[Cr(III)(acac)$_3$]	d^3	(+) at 1464 cm^{-1} A$_2$-mode[c]	(−) at 1462 cm^{-1} degenerate E-mode[b]	A$_2$ (ip) > E (oop)
Δ-[Ru(III)(acac)$_3$][d]	d^5	(+) at 1457 cm^{-1} A$_2$-mode[c]	(−) at 1402 cm^{-1} E-mode[e]	A$_2$ (ip) > E (oop)

[a] ip, in-phase; oop, out-of-phase. [b] Scheme 1b,c. [c] Scheme 1a. [d] The assignment is done with the assumption that [Ru(III)(acac)$_3$] approximately belongs to D_3 symmetry. [e] Scheme 1b.

Table 4. Calculated Effects of the Central Metal Ion of Δ-[M(III)(acac)$_2$(dbm)] on VCD Spectra of C−O Vibrations

complex with C_2 symmetry	config	sign of split peaks of C−O stretching, assignment: higher frequency	sign of split peaks of C−O stretching, assignment: middle frequency	sign of split peaks of C−O stretching, assignment: lower frequency	order of vibration modes in frequency[a]
Δ-[Co(III)(acac)$_2$(dbm)]	d^6	(−) at 1473 cm^{-1} A-mode[b]	(+) at 1471 cm^{-1} B-mode[c]	(+) at 1463 cm^{-1} B-mode[d]	A (oop) > B (oop) > B (ip)
Δ-[Cr(III)(acac)$_2$(dbm)]	d^3	(+) at 1463 cm^{-1} B-mode[d]	(−) at 1461 cm^{-1} A-mode[b]	(−) at 1451 cm^{-1} B-mode[c]	B (ip) > A (oop) > B (oop)
Δ-[Ru(III)(acac)$_2$(dbm)]	d^5	(−) at 1465 cm^{-1} A-mode[b]	(+) at 1452 cm^{-1} B-mode[d]	(−) at 1397 cm^{-1} B-mode[c]	A (oop) >B (ip) > B (oop)

[a] ip, in-phase; oop, out-of-phase. [b] Scheme 2c. [c] Scheme 2b. [d] Scheme 2a.

and A (−) > B (+) > B (−) for Δ-[Ru(III)(acac)$_2$(dbm)]. Thus, in the case of these bis(chelated) complexes, too, the order of energy levels is influenced by the central metal ion in a symmetry-dependent way. Table 4 summarizes the calculated C−O stretches at 1500−1300 cm^{-1} of [M(III)(acac)$_2$(dbm)].

To summarize the above results, the VCD bands of a chiral metal complex are influenced by the central metal under the following conditions: (i) at least one of the atoms in a concerned vibration is bonded with a metal ion or (ii) a concerned band is a composite of several peaks with different symmetries.

It is interesting to examine how the lowering of symmetry from D_3 to C_2 affects the spectral properties of VCD. Table 5 summarizes the correlation of vibrational modes between tris- and bis(acetylacetonato)metal(III) complexes. From the comparison of interligand correlative vibrational motions (Schemes 1 and 2), it is deduced that the A$_2$-mode in [M(III)(acac)$_3$] corresponds to the B- (in-phase) mode in [M(III)(acac)$_2$(dbm)], while the doubly degenerate E-mode in [M(III)(acac)$_3$] splits into the B- (out-of-phase) and A- (out-of-phase) modes in [M(III)(acac)$_2$(dbm)]. When the VCD spectra are compared between these two complexes for the same type of central metal, the sign of the A$_2$-mode is retained for the B- (in-phase) mode for the investigated three complexes (Co, Cr, and Ru). The sign of the E-mode is also retained for the B- (out-of-phase) and A- (out-of-phase) modes except for the B- (out-of-phase) mode in the case of [Co(III)(acac)$_2$(dbm)].

The sign and intensity of a peak in the VCD spectrum are determined by rotational strength, R, as given by $R = \{\mathrm{Im}\}(\mu\cdot m)$, where μ and m are the electric and magnetic dipole transition moments, respectively. Thus, in most cases, the electronic configuration of the central metal ion has little effect on the signs of both μ and m when the symmetry of the complex is lowered from D_3 to C_2. It is not very clear why the Co(III) complex alone inverts the sign of the B- (out-of-phase) mode by replacing one of the acac ligands with dbm. The electronic configuration of d-electrons in a central metal ion might affect in a delicate way the sign of the magnetic transition moment (m). As far as we know, there has been no systematic study correlating the VCD spectra for a series of tris(chelated) complexes in which a ligand in the parent complex is replaced successively with a ligand of a different kind. Such a study may be helpful to establish a general rule for the correlations of VCD spectra when the symmetry of a complex is lowered from D_3 to C_2.

In this work, magnetic field perturbation (MFP) theory has been extended to open-shell systems such as Cr(III) and Ru(III) complexes. There is no theoretical reason to avoid such extension as far as the system is appropriately described by the electronically ground state. It is, of course, even more difficult to treat an open-shell system by the above theory, since the spin multiplicity causes a number of energetically close electronic states. Our application of the theory is regarded as considering a single dominating state among these states. The validity of such treatment may be judged by comparing the calculated results with the observed ones. In this sense, the fact that the calculated results well reproduce the observed ones in both Cr(III) and Ru(III) complexes is thought to validate the present approach. The work provides a benchmark of VCD application for open-shell transition metal cases. It is certain that the broad band below 1300 cm^{-1} for Ru(III) complexes arises from the low-lying excited states involving d−d transitions. It is our fortune that the intensity of that band is much less than

Table 5. Correlation of Vibrational Modes between Tris- and Bis(acetylacetonato)metal(III) Complexes

Central metal ion	$[M(III)(acac)_3]$		$M(III)(acac)_2(dbm)]$
	A_2 (in-phase)	→	B(in-phase)
	E (out-of-phase)	→	B(out -of-phase)
		↘	A (out-of-phase)
Central metal ion	**Δ−$[M(III)(acac)_3]$**		**Δ−$[M(III)(acac)_2(dbm)]$**
Co (III)	(+) A_2 (in-phase)	→	(+) B(in-phase)
	(-) E (out-of -phase)	→	(+)B(out -of- phase)
		↘	(-) A(out-of -phase)
Cr (III)	(-) E (out-of-phase)	→	(-) B(out-of -phase)
	(+) A_2 (in -phase)	→	(-) A(out-of-phase)
		↘	(+) B(in-phase)
Ru (III)	(-)E (out-of-phase)	→	(-)B(out-of-phase)
	(+)A_2 (in-phase)	→	(+)B(in- phase)
	(-)E (out-of-phase)	→	(-) A(out-of-phase)

previously observed in Ni(II) and Co(II) complexes.[29] Thus we regard that such an effect does not affect crucially the VCD features of C−O stretches.

Conclusion

This paper reports the experimental vibrational circular dichroism (VCD) spectra of two different series of chiral tris(β-diketonato) complexes. With the help of theoretical works based on the magnetic field perturbation (MFP), the results are rationalized in terms of the effect of the central metal ion on the energies of the correlative vibrations of ligands. Detailed assignment of composite peaks as performed in the present study is impossible by IR spectroscopy alone. In this sense, VCD spectroscopy has enabled us to observe directly the effect of the metal ion on determining the vibration energy levels concerning the correlative motions among vicinal ligands.

Experimental Section

[M(III)(acac)]. $[Co(III)(acac)_3]$, $[Cr(III)(acac)_3]$, $[Ru(III)(acac)_3]$, $[Rh(III)(acac)_3]$, and $[Ir(III)(acac)_3]$ were purchased from Kanto Kagaku Co. Ltd. These complexes were chromatographically resolved in methanol as described below. The concentration of an enantiomer was determined spectrophotometrically by use of ϵ and $\Delta\epsilon$ values reported in the literature.[49]

Synthesis of $[Co(III)(acac)_2(dbm)]$. $[Co(III)(acac)_3]$ (0.80 g, 2.2 mmol) and dbmH (0.50 g, 2.2 mmol) were dissolved in dichloromethane under nitrogen. BF_3-CH_3COOH (0.14 mmol) was added slowly, and the mixture was stirred at room temperature for 24 h.[50]After the reaction, a 10% CH_3COOK solution (10 mL) was added and the mixture was extracted with ether (200 mL). The solution was evaporated and a crude product was purified on a silica gel column with a mixture of benzene−acetonitrile (10:1) as an eluent. Yield: 0.30 g (27%). The fraction was further purified on a reversed-phase HPLC column (2 mm i.d. × 250 mm) (Capcell Pack, Shiseido Ind. Co., Japan) by being eluted with acetonitrile−water. FAB-MS (*m/z*) calcd for $[M]^+$ 480.4, found 480. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.92 (d, $J = 7.6$ Hz, 4H), 7.46 (t, $J = 7.6$ Hz, 2H), 7.38 (t, $J = 7.6$ Hz, 64H), 6.77 (s, 1H), 5.62 (s, 2H), 2.99 (s, 6H), 2.17 (s, 6H). Anal. Calcd for $C_{25}H_{25}O_6Co$: C, 62.50; H, 5.25. Found: C, 62.08; H, 5.33.

Synthesis of $[Cr(III)(acac)_2(dbm)]$. $[Cr(III)(acac)_3$](0.70 g; 2.0 mmol) and dbmH (0.44 g; 2.0 mmole) were mixed in solid form and kept in an autoclave for 16 h at 160 °C. The brown crude product was eluted from a silica gel column (30 mm i.d. × 600 mm) with acetonitrile−benzene. Yield: 0.25 g (26%). The fraction was further purified on a reversed-phase HPLC column (2 mm i.d. × 250 mm) (Capcell Pack, Shiseido Ind. Co., Japan) by being eluted with acetonitrile−water. FAB-MS (*m/z*) calcd for $[M]^+$ 473.46, found 473. Anal. Calcd for $C_{25}H_{25}O_6Cr$: C, 63.42; H, 5.32. Found: C, 62.43; H, 5.42.

Synthesis of $[Ru(III)(acac)_2(dbm)]$.[8a] $[Ru((III)(acac)_2(CH_3CN)_2]$-$ClO_4$ (0.18 g; 0.40 mmol), dbmH (0.09 g; 0.40 mmol), Zn powder (0.053 g), and $KHCO_3$ (0.059 g) were dissolved in 40 mL of ethanol and 2 mL of water, and the solution was refluxed overnight. The solution was cooled, filtered through Celite, and evaporated. The residue was dissolved in 50 mL of chloroform, and the solution was refluxed overnight again with 5−10 mL of an aqueous solution containing 0.1−0.2 g of $AgNO_3$ added. The solution was evaporated to dryness and purified by HPLC (Shiseido Capcell Pak C18). Yield: 38% of a deep red powder, mp 240 °C (decomp). FAB-MS (*m/z*) calcd for $[M]^+$ 522.5, found 523. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.82 (d, $J = 6.7$ Hz, 4H), 9.96 (t, $J = 7.0$ Hz, 2H), 6.58 (m, 4H), −2.46 (s, 6H), −4.87 (s, 6H), −27.58 (s, 2H), −40.97 (s, 1H). Anal. Calcd. for $C_{25}H_{25}O_6Ru{\cdot}1.5H_2O$: C, 54.64; H, 5.12. Found: C, 54.14; H, 4.94.

Resolution of $[M(III)(acac)_3]$ and $[M(III)(acac)_2(dbm)]$. Optical resolution was performed on a chiral column packed with an

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Table 6. Absorption and CD Spectra of Δ-[M(III)(acac)$_2$(dbm)] in Methanol

complex	λ, nm	ϵ, mol^{-1} cm^{-1}	$\Delta\epsilon$, mol^{-1} cm^{-1}
Δ-[Co(III)(acac)$_2$(dbm)]	597	183.4	−5.09
Δ-[Cr(III)(acac)$_2$(dbm)]	560	80.5	−2.68
Δ-[Ru(III)(acac)$_2$(dbm)]	500	1902	+ 4.66

ion-exchange adduct of Δ-[Ru(phen)$_3$]$^{2+}$ (phen = 1,10-phenanthroline) and synthetic hectorite (Ceramosphere RU-1, Shiseido Ind. Co.) with methanol.[51] The Λ and Δ isomers were resolved in the baseline separation in this order. Measured ϵ and $\Delta\epsilon$ values are summarized for [M(III)(acac)$_2$(dbm)] in Table 6.

Instruments. CD spectra were recorded on a JASCO J-720 spectropolarimeter. The VCD spectra were recorded at a 4 cm^{-1} resolution using a circular spectrometer JV-2001 (JASCO, Japan) and Bomem/BioTools, Inc.[41] For the measurements, a CDCl$_3$ solution of a complex (ca. 0.04 M) was injected into a cell (6.2 cm^2 × 100 μm) with CaF$_2$ windows. The signal was accumulated with 3000 scans for tris-chelated complexes and 10 000 scans for bis-chelated complexes during about 30 min and about 2 h, respectively. IR absorbance adjusted under 1.0 was optimal for VCD measurements. The mole concentration of each metal complex was 0.04 M.

Calculation Details. The VCD spectra of these complexes were theoretically calculated for their optimized geometries. Vibrational frequencies and VCD intensities were simulated by use of Gaussian 03 at the DFT level [B3LYP functional with LANL2DZ for transition metals and 6-31G(d) for other atoms].[52] Co(III) $(e_g)^6$, Rh(III) $(e_g)^6$, Ir (III) $(e_g)^6$, and Al(III) were specified as singlet in the closed-shell system, while Cr(III) $(e_g)^3$ and Ru(III) $(e_g)^5$ were specified as quartet and doublet in the open-shell system, respectively. [M(III)(acac)$_3$] was assumed to have D_3 symmetry for M = Co, Cr, Rh, Ir, and Al and to have C_2 symmetry for M = Ru.[45,53] The reason that the C_2 symmetry was selected for [Ru(III)(acac)$_3$] instead of D_3 was that the energy was not converged under the assumption of D_3 symmetry. This was probably because the Jahn−Teller distortion from D_3 symmetry is not neglected for this Ru(III) complex. The same calculation was previously reported by other authors.[53] [M(III)(acac)$_2$(dbm)] was assumed to have C_2 symmetry. IR and VCD spectra were calculated after the geometry optimization. The optimization was performed with tight convergence, avoiding numerical errors. No correction of introducing a scale factor, however, was made in the present calculation. VCD intensities were determined by the vibrational rotational strength and magnetic dipole moments, which were calculated by the magnetic field perturbation method with gauge-invariant atomic orbitals.[14] Description of calculated modes is based on the animations of the modes and spectra to the resolution of 1 cm^{-1} with Gauss view 3.09 (Gaussian Inc.).

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Supporting Information Available: Results of ECD of [M(III)(acac)$_3$] (M = Co, Rh, Ir, Cr, and Ru)and of chromatographic resolution of [M(III)(acac)$_2$(dbm)] (M = Co, Cr, and Ru)and assignment of the main peaks of IR and VCD spectra of [M(IIII)-(acac)$_3$] and [M(III)(acac)$_2$(dbm)]. This material is available free of charge via the Internet at http://pubs.acs.org.

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