Dramatic Effects of d-Electron Configurations on Vibrational Circular Dichroism Spectra of Tris(acetylacetonato)metal(III)

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The VCD spectra of a series of tris(acetylacetonato)-metal(III) ([M(acac)$_3$] with M = Co, Cr, Ru, and Rh) have revealed a new aspect concerning the effects of a central metal ion on the vibrational energy levels split by the inter-ligand interactions. Our present view is that the correlated vibrational motions of vicinal ligands are affected by the d-electron configuration of a central metal ion.

Vibrational circular dichroism (VCD) measures the differential absorption of left versus right circularly polarized IR radiation by a molecular vibration transition. When it is applied to metal complexes, the method may provide a powerful tool for examining the stereochemical details in coordination structures.[1–3] The pioneering works by Nafie et al., for example, report the VCD spectrum of various kinds of metal complexes such as [bis(acetylacetonato)(l-alaninato) cobalt(III)]. The analyses of the spectra revealed the details of coupled oscillator interactions among the ligands.[4]

Motivated by those works, we have measured the VCD spectra of a series of tris(acetylacetonato)metal(III) ([M(acac)$_3$] with M = Co, Cr, Ru, and Rh). As a result, we report a new aspect concerning the role of d electrons of a central metal ion in the VCD spectra. Our present view is that the symmetry of the d-electron configuration has a decisive effect on the energy of vibrational levels split by the correlated motions of vicinal ligands.

[M(acac)$_3$] was optically resolved by being eluted on a HPLC column packed with an ion-exchanged adduct of Δ-[Ru(phen)$_3$]$^{2+}$ and synthetic hectorite (Ceramosphere RU-1, Shiseido Co., Ltd., Japan).[5,6] When a racemic mixture was eluted by methanol, the Λ- and Δ-enantiomers were separated as less and more retaining enantiomers, respectively, in all investigated cases. The absolute configuration of an eluted molecule was determined on the basis of its CD spectrum in methanol.[7]

Figures 1a–1d show the VCD and FTIR spectra for [M(acac)$_3$] with M = Co, Cr, Ru, and Rh, respectively. All of four complexes gave similar FTIR spectra in the whole range (1000–1700 cm^{-1}). When the VCD spectra are compared, nearly the identical spectra are seen in the range of 1700–1500 cm^{-1}, which corresponds to the C–C stretching vibrations. Notably quite different features appear in the range of 1500–1300 cm^{-1}, which corresponds to the C–O vibrations. In this frequency region, the spectra consist of the oppositely signed two peaks for all the investigated complexes. These two peaks were caused by the splitting of vibrational energy level due to the interaction of vicinal ligands.[4] In case of the Δ-enantiomers of [Co(acac)$_3$] and [Rh(acac)$_3$] (denoted as *group I*), the negative peak appears at the higher frequency with the residual positive peak at the lower frequency. Naturally all peaks invert their signs for the Λ-enantiomer. In contrast to this, the Δ-enantiomers of [Cr(acac)$_3$] and [Ru(acac)$_3$] (denoted as *group II*) showed the positive peak at the higher frequency with the negative peak at the lower frequency. In other words, the bisignate nature of the split bands of C–O stretching was opposite between *groups I* and *II*. Since the FTIR spectra were similar among the investigated metal complexes, the reasons for the observed difference in the VCD spectra should be sought in the detailed electronic configuration of a central metal ion for these groups.

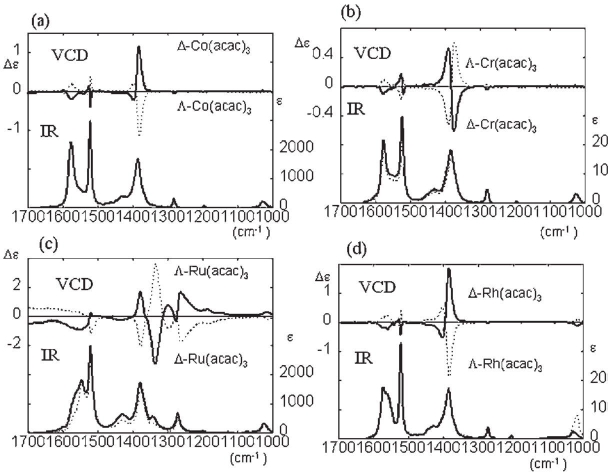


Figure 1. The observed FT-IR (lower) and VCD (upper) spectra of M(acac)$_3$; M = (a) Co, (b) Cr, (c) Ru, and (d) Rh. The solid and dotted curves correspond to the Δ- and Λ-enantiomers, respectively.

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 program at the DFT level (B3LYP functional with LANL2DZ for transition metal and 6-31G(d) for other atoms).[8] As is shown in Figures 2a–2d, the calculated results of Δ-isomers well reproduce the observed ones for all of the investigated complexes except for the shift of the peak position towards higher frequency.[9] The facts imply that the observed features of the VCD spectra should be interpreted within the magnetic field perturbation theory in which the role of d electrons is taken into account.

According to Nafie et al., the bisignate nature of the small peaks around 1500 cm^{-1} originates from the coupled oscillator mechanism for the in-plane C–C stretching mode of two acetylacetonato lignads. Two modes were assigned as the "S" (synchronized phase) mode and "A" (antisynchronized phase) mode, respectively. Their signs and relative energy positions

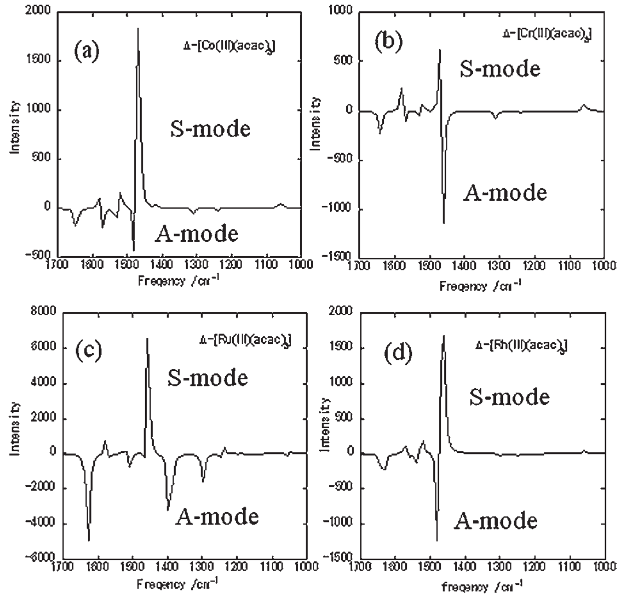
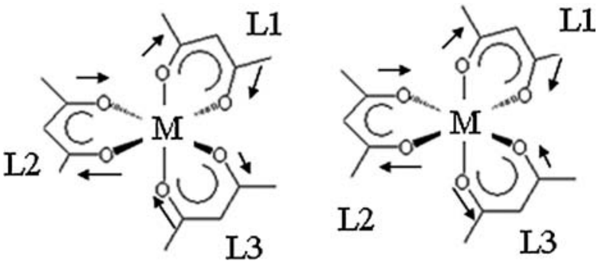


Figure 2. The calculated VCD spectra of Δ-M(acac)$_3$; M = (a) Co, (b) Cr, (c) Ru, and (d) Rh. No correction of introducing a scale factor was made for these spectra.[9]



(a) S-mode (b) A-mode

Figure 3. Schematic drawings of S- and A-modes in the C–O vibrations. (a) S-mode: L1, L2, and L3 are all in phase; (b) A-mode: L1 and L2 are in phase, while L3 is out of phase.

are interpreted successfully on the basis of the coupled oscillator model. In the present cases, the VCD spectra in the in-plane C–C region are nearly the same for the investigated complexes. Therefore, the interligand coupling is unaffected by the electronic properties of a central metal ion as far as the C–C vibrational mode is concerned.

In contrast to the C–C vibrational mode, the remarkable difference in the spectral shape was observed for the C–O stretching vibration (1500–1300 cm^{-1}) among the complexes. When the vibronic motions of ligands in the Δ-enantiomers are studied in detail, it is deduced that the peak with a negative sign corresponds to the C–O vibration in which two of the three acetylacetonato ligands are in the same phase, while the rest of the ligands is out of phase (as denoted by A-mode in Figure 3). The peak with a positive sign corresponds to the vibration in which three of the ligands are all in the same phase (as denoted by S-mode in Figure 3). These situations are valid for all metal complexes. Thus, the observed features in this C–O stretching region among metal complexes can be rephrased by a rule that the vibrational energy of A-mode is higher than that of S-mode in case of Δ-enantiomers of *group I* (Co(III) and Rh(III)), while the energy relation is reversed for the same enantiomers of *group II* (Cr(III) and Ru(III)). A key aspect of the observed electronic effect might lie in the fact that Co(III) ((e_g)^6) and Rh(III) ((e_g)^6) have the diamagnetic d-electron configuration, while Cr(III) ((e_g)^3) and Ru(III) ((e_g)^5) have the paramagnetic d-electron configuration. According to our present view, the diamagnetic configuration or probably the symmetric distribution of d-electron densities stabilizes more the in-phase motion of vicinal ligands than the out-of-phase motion, while the situations are reversed for the asymmetric distribution of d-electron densities.

Apart from the validity of the details in the above proposal, this is at least a definite evidence for the effects of d-electron configurations on the VCD spectra of a metal complex. In this sense, the VCD spectroscopy is effective in revealing the participation of d-electrons in the vibrational details.

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References

1 Y. He, X. Cao, L. A. Nafie, T. B. Freedman, *J. Am. Chem. Soc.* **2001**, *123*, 11320.
2 K. Monde, T. Taniguchi, N. Miura, S.-I. Nishimura, *J. Am. Chem. Soc.* **2004**, *126*, 9496.
3 T. Taniguchi, N. Miura, S.-I. Nishimura, K. Monde, *Mol. Nutr. Food Res.* **2004**, *48*, 246.
4 D. A. Young, E. D. Lipp, L. A. Nafie, *J. Am. Chem. Soc.* **1985**, *107*, 6205.
5 A. Yamagishi, *Rev. Coord. Chem.* **1987**, *16*, 131.
6 J. Yoshida, H. Sato, A. Yamagishi, N. Hoshino, *J. Am. Chem. Soc.* **2005**, *127*, 8453.
7 A. F. Drake, J. M. Gould, S. F. Mason, C. Rosin, F. J. Woodely, *Polyhedron* **1983**, *2*, 537.
8 M. J. Frisch, et al. *Gaussian 03, Revision B.03*, Gaussian, Inc., Pittsburgh, PA, **2003**.
9 T. B. Freedman, X. Cao, R. K. Dukro, L. A. Nafie, *Chirality* **2003**, *15*, 743. A scale factor of 0.97 is typically used for the frequencies calculated by DFT(B3LYP/6-31G(d)).