Vibrational Circular Dichroism in Bis(acetylacetonato)(L-alaninato)cobalt(III). Isolated Occurrences of the Coupled Oscillator and Ring Current Intensity Mechanisms

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Abstract: Vibrational circular dichroism spectra have been obtained for Δ- and Λ-bis(acetylacetonato)(L-alaninato)cobalt(III) in the hydrogen stretching region between 3400 and 2800 cm⁻¹ and the mid-infrared region between 1600 and 1180 cm⁻¹. The bisignate VCD spectrum centered at 1522 cm⁻¹, due to the doubly degenerate antisymmetric CC stretching mode of the acetylacetonato rings, is interpreted on the basis of the coupled oscillator intensity mechanism. Remaining VCD features are explained primarily in terms of vibrational currents in rings formed by an intramolecular hydrogen bond or transition-metal ligation. It is shown, based on the appearance of a large negative VCD band in the NH stretching region of the Δ complex, which does not appear in the Λ complex, that an intramolecular hydrogen bond forms between the L-alaninato ligand and one of the acetylacetonato ligands in the Δ complex but forms only weakly if at all in the Λ complex.

In recent years vibrational circular dichroism (VCD) has emerged as a sensitive new technique for the study of stereochemical details of chiral molecules in dispersed media. The growth in the number and variety of VCD spectra that have been measured has spurred efforts to gain a more complete understanding of the theoretical basis of VCD intensities and to establish correlations between observed VCD features and details of molecular structure and conformation. Due to difficulties in the formal description of VCD intensities, approximate theoretical models of various types have played a role in the development of VCD. Early theoretical models focused on the nuclear displacements associated with vibrational motion as the fundamental descriptors of VCD intensity. More recent models have attempted to take into account the motion of electronic charge density as a correlated, yet distinct, form of intensity contribution.

Perhaps the simplest of all models of VCD intensity is the degenerate coupled oscillator model.[2] In its most elementary form, local magnetic moment contributions are ignored and the model describes the coupling of a pair of degenerate electric transition moments that are skewed dissymmetrically with respect to one another. Another simple model, the fixed partial charge (FPC) model,[3] describes VCD intensity in a normal mode as the sum of all pairwise contributions of nuclear displacements. Since the mathematical form of these contributions is the same as the form of the VCD intensity described by the coupled oscillator model, the FPC model can be regarded as a generalization of the coupled oscillator model to the description of VCD from nuclear displacements in vibrational normal modes. Both the FPC model and the coupled oscillator model are based on the coupling of electric moments that arise directly from the nuclear motion

without a separate contribution from the associated motion of electron density.

A number of models of VCD intensity have now been developed that take into account in an explicit fashion the contribution of electronic motion to the calculated intensity. They are the localized molecular orbital model,[4] the charge flow,[5] and closely related nonlocalized molecular orbital[6] models, the atomic polar tensor model,[7] the dynamic polarization model,[8] and the bond dipole model.[9] The specific aspect of VCD intensities that has led to the extensive use of various models is the vanishing of the electronic contribution to the vibrational magnetic dipole transition moment within the Born–Oppenheimer approximation for a molecule with a nondegenerate ground electronic state.[10] Recently, we have developed expressions through the use of vibronic coupling formalism to describe these missing contributions of the electronic motion. Although these expressions lie beyond the Born–Oppenheimer approximation they are adiabatic in form, i.e., the expressions can be factored into separate nuclear and electronic parts. These non-Born–Oppenheimer vibronic coupling terms describe the correlation of electronic current density in molecules that is induced by the momenta of the nuclei during vibrational motion.[11] Such a correlation is the momentum analogue of the spatial correlation between electron density and nuclear positions that is the basis of the Born–Oppenheimer approximation.

A particularly intriguing aspect of vibrationally induced electronic currents in molecules is the possible occurrence of rings of electronic current. In a molecule that possesses an intramolecular ring with delocalizable charge density, a ring current could be induced by vibrational motion within the ring itself or adjacent to it. Such a current would oscillate about an average value of zero current in phase with the vibrational motion. Since the

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current would be largely unaccompanied by nuclear motion, the resulting magnetic moment and contribution to VCD intensity could be quite large. In addition, at least a component of the ring current could be regarded as occurring throughout the ring at constant electron density. Such a component would not contribute to the electric dipole transition moment, and hence to the ordinary absorption, and would not produce any redistribution or polarization of electronic charge density in the ring.

Recently, we proposed the existence of a ring current mechanism that contributes large positive VCD intensity in the CH stretching region for most of the naturally occurring L-amino acids, some of their bis-amino acid copper(II) complexes, and one cobalt(III) complex.[12] For all of these molecules, a large positive VCD bias is observed in the CH stretching region. The bias is attributed to the presence of vibrationally generated electronic current density in the intramolecular ring formed by a hydrogen bond between the amine and carboxylic acid groups in the case of the amino acids or the ligand–transition-metal bonds in the case of the transition-metal complexes.

Starting from the simplest amino acids, such as alanine and its CH-deuterated analogues, a detailed interpretation of these amino acid VCD spectra has been constructed. Although some of the spectra in this series are rather complex and represent the superposition of VCD contributions of many CH stretching normal modes, two principal VCD intensity mechanisms have been identified. One is the coupling of the various CH stretching electric dipole moments that can be adequately described by a nuclear motion VCD model such as the FPC model or, in especially simple cases, the coupled oscillator model. This nuclear motion mechanism applies to nearly all of the CH stretching modes in the amino acid. A theoretical consequence of the application of nuclear motion models to the CH stretching of the amino acids is the absence of a bias in the VCD spectra to either positive or negative intensity. In other words, the sum of the VCD intensity in this region is predicted to be nearly zero.

The other VCD mechanism is associated with the large, positive VCD bias observed in this region that arises from the stretching of the C_α–H methine bond. The positive VCD intensity arises from the combination of the electric dipole moment aligned with the C_α–H bond and a magnetic moment induced by a current in the intramolecular ring described above. The structural and vibrational elements associated with this intensity mechanism are the same for all of the L-amino acids and their transition-metal complexes. It is observed that the VCD bias is nearly the same for the amino acids investigated and approximately a factor of 2 per amino larger for the transition-metal complexes. The regularity for the amino acids follows from the absence of a direct side-chain contribution to the C_α–H driven ring current mechanism. The enhancement for the metal complexes is attributed to an increased ring current which now includes contributions from the transition metal, to a more favorable geometry between the inducing C_α–H oscillator and the intramolecular ring, or to lower conformational mobility in the complexes.

Further considerations of these two intensity mechanisms as applied to other VCD spectra have led us to regard the two mechanisms as having widespread utility in the interpretation of VCD spectra, particularly where intramolecular associations are thought to be present.[13] While several instances of the clear applicability of the coupled oscillator model[14] and the fixed partial charge model[15] have appeared in the literature, a similar un-
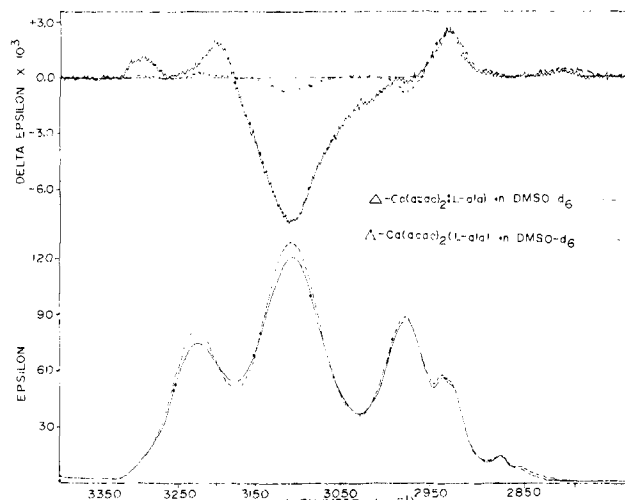

Figure 1. Absorption and VCD spectra of Δ- and Λ-Co(acac)₂(L-alaninato) in Me₂SO-d_6 solution in the hydrogen stretching region. The concentrations and path lengths for the Δ and Λ complexes were 0.27 M at 200 μm and 0.33 M at 150 μm, respectively.

equivocal demonstration of the ring current mechanism has yet to be presented.

The VCD spectra of Δ- and Λ-bis(acetylacetonato)₂(L-alaninato)cobalt(III) in the NH stretching region constitute an exceptionally clear example of the occurrence of the ring current intensity mechanism of VCD intensity. Coincidentally, these complexes also exhibit a particularly striking example of the coupled oscillator mechanism of VCD in the mid-infrared region. In addition, they possess nearly equal, positively biased VCD spectra in the CH stretching region which arise from the ring current intensity mechanism previously reported for amino acids and their transition-metal complexes.[12]

Experimental Section

Preparations and Optical Resolutions. The Δ and Λ diastereomers of the Co(acac)₂(L-alaninato) and Co(acac)₂(D-alaninato) complexes (acac = acetylacetonato) were prepared from Na[Co(acac)₂(NO₂)₂] and the separate enantiomers of alanine according to the procedure published by Laurie.[16] Separation of the optically active Δ and Λ diastereomers was accomplished by column chromatography on aluminum oxide and elution with ethyl acetate–ethanol mixtures as described by Seematter and Brushmiller.[17] The purities of the diastereomers were established by measurement of the integrated areas of their methine proton NMR signals. The diastereomers had optical purities ranging from 80 to 90%. In addition to their proton NMR spectra, the UV–vis, IR, and electronic CD spectra of all the diastereomers were in excellent agreement with those reported in the literature.[16,17]

Co(acac)₃ was prepared by the method of Bryant and Fernelius.[18] The racemic mixture was partially resolved by column chromatography. The method described by Jonas and Norden[19] was used. A column was filled with aluminum oxide and D-lactose, and the sample was eluted with a mixture of benzene and hexane. Both enantiomers were obtained in 45% enantiomeric excess, as determined by comparison of their electronic CD spectra to values reported in the literature.[20,21]

Spectra. Two VCD spectrometers were used in this investigation. All of the spectra above 2700 cm⁻¹ were obtained with a dispersive VCD instrument constructed at Syracuse University and described previously.[22] All of the spectra below 1600 cm⁻¹ were measured with a Nicolet 7199 FT–IR spectrometer according to the details presented elsewhere.[23]

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Table I. Frequencies (cm^{-1}), Intensities (cm^{-1} L mol^{-1}), and Assignments for the Absorption and VCD Spectra of Δ-Co(acac)$_2$(L-alaninato)^a in Me$_2$SO-d_6

absorption spectra		VCD spectra		
frequency	intensity	frequency	intensity $\times$ 10^3	assignment
3239	75 (82)	3300	+1.5 (+0.2)	$\nu^a_{NH_2}$
		3215	+2.0 (+0.3)	
3105	120 (130)	3110	-8.0 (-1.0)	$\nu^s_{NH_2} + \nu_{CH}(acac)$
2976	88 (90)	2980	-0.3 (-1.0)	$\nu^a_{CH_3}(ala, acac)$
2934	58 (60)	2930	+2.5 (+2.5)	$\nu^s_{CH_3}(ala, acac) +$ $\nu_{C_\alpha\cdot H}(ala)$
2925	55 (57)			
2875	15 (15)			$2 \times \delta^a_{CH_3}(ala)$
2855	8 (10)			$2 \times \delta^a_{CH_3}(acac)$
1585	800 (800)	1570	+25 (-15)	$\nu^a_{CO}(acac)$
1576	1100 (1800)			
1522	1800 (1800)	1524	+45 (-45)	$\nu^a_{CC}(acac)$
		1520	-38 (+38)	
1456	250 (250)	1456	-10 (+10)	$\delta^a_{CH_3}(ala)$
1434	300 (300)	1434	0 (0)	$\delta^a_{CH_3}(acac)$
1390	1150 (1150)	1396	-70 (+80)	$\nu^s_{CO}(ala, acac)$
1378	750 (750)	1377	+140 (-30)	$\delta^s_{CH_3}(ala, acac)$
1348	250 (250)	1348	+40 (-80)	$\delta_{C_\alpha\cdot H}(ala)$
1282	325 (325)	1282	+20 (-40)	$\delta_{CH}(ala, acac)$
1220	200 (200)			
1200	225 (225)			

^{a} Intensities for the Λ complex are given in parentheses.

Optical filtering was necessary to prevent detector saturation in the FT–VCD measurements. A long-pass infrared filter from Optical Coatings Laboratory, Inc. was used to remove light above 1600 cm^{-1}.

The VCD and IR spectra were recorded as solutions in either Me$_2$SO-d_6 or CDCl$_3$. A variable path length cell with calcium fluoride windows was used for all measurements. The base line for each VCD spectrum was taken as the average of two enantiomer spectra. This process eliminates absorption artifacts and removes the polarization sensitivity of the optical system. The VCD spectra were multiplied by the appropriate factors so that they correspond to samples of 100% optical activity. IR absorption spectra are presented after removal of solvent bands by spectral subtraction.

Electronic absorption spectra were recorded on a Varian Cary 219 UV–vis spectrophotometer. Electronic CD spectra were measured with a Jasco CD spectropolarimeter which was calibrated with aqueous solutions of camphorsulfonic acid-d_{10}. Proton NMR spectra were obtained with a Bruker wide-bore 360-MHz Fourier transform NMR spectrometer.

Results

Hydrogen Stretching Spectra. The VCD and absorption spectra in the NH and CH stretching regions of Δ- and Λ-Co(acac)$_2$(L-alaninato) dissolved in Me$_2$SO-d_6 are presented in Figure 1. Provided in Table I are listings of the observed frequencies and intensities of the VCD and absorption maxima, as well as a general assignment for the normal mode or modes associated with the observed bands. The broad absorption bands at 3239 and 3105 cm^{-1} are assigned to the antisymmetric and symmetric NH$_2$ stretching modes of the alaninato ligand, although the latter band also contains the methine CH stretching mode of the acac ligand. Although the intensity of this CH stretching mode is weak and is not observed directly, the stretching frequency of lone CH oscillators that are part of a π system have been calculated to occur near 3085 cm^{-1} by Behnke and Nakamoto.[24] The band at 2976 cm^{-1} is assigned to the antisymmetric methyl stretching modes of both the acac and alaninato ligands. The two bands that are just resolved at 2934 and 2925 cm^{-1} are assigned to three modes: the two symmetric methyl stretching modes of the acac and alaninato ligands and the methine CH stretching mode of the alaninato ligand. The methine band is generally broad with low peak intensity and hence is most likely not one of the two observed peaks. The two weak bands below 2900 cm^{-1} are assigned as Fermi enhanced overtones of the methyl antisymmetric deformation modes of the alaninato and acac ligands.

The absorption intensities of the Δ and the Λ complexes are virtually the same in the CH stretching bands below 3000 cm^{-1}

Table II. Frequencies (cm^{-1}), Intensities (cm^{-1} L mol^{-1}), and Assignments for the Absorption and VCD Spectra of Δ-Co(acac)$_2$(L-alaninato)^a in CDCl$_3$ Solution

absorption spectra		VCD spectra		
frequency	intensity	frequency	intensity $\times$ 10^3	assignment
3348 (3351)	82 (90)	3350	+4.5 (+1.0)	$\nu^a_{NH_2}$
3290 (3290)	52 (65)	3385	-5.0 (-1.0)	$\nu^a_{NH_2}$
3090 (3090)	4 (4)			$\nu_{CH}(acac)$

^{a} Frequencies and intensities for the Λ complex are given in parentheses.

and very nearly the same in the predominantly NH stretching bands above that frequency. The NH stretching bands of the Δ complex are slightly less intense, slightly broader, and slightly lower in frequency than those of the Λ complex. Likewise, the VCD intensities are virtually the same for the two complexes below 3000 cm^{-1}; however, above this frequency the VCD intensities of the Δ complex are an order of magnitude larger than those of the Λ complex, even though the maxima, minima, and zero crossings of the two VCD spectra correspond closely.

The assignment of the VCD spectra parallels that of the absorption spectra with the following additional aspects. The VCD associated with the antisymmetric NH$_2$ stretching mode appears as two bands that are rather widely separated in frequency. It is proposed that the overtone of the NH$_2$ scissors mode, the fundamental of which occurs above 1600 cm^{-1} but is obscured by solvent bonds, is located within the NH$_2$ antisymmetric stretching band and borrows negative VCD intensity from the neighboring NH$_2$ symmetric stretching band through Fermi resonance interaction. This type of Fermi resonance interaction has been observed in acetamide dissolved in strongly hydrogen bonded solvents such as Me$_2$SO or pyridine.[25] The negative VCD from this presumably narrower overtone band then diminishes the central portion of the main VCD band, thus dividing its intensity. Another point of interest is the identical VCD maxima of both complexes at 2930 cm^{-1}. The origin of this band, based on earlier studies of VCD in amino acids and their complexes,[12] is almost certainly the methine CH stretching mode of the alaninato ligand.

The VCD and absorption spectra for these complexes as solutions in deuterated chloroform are presented in Figure 2. The low solubility of these complexes in CDCl$_3$ precluded VCD

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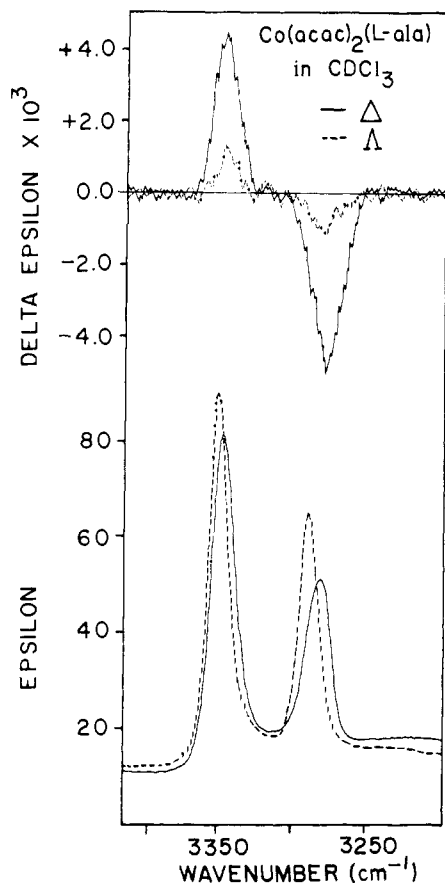
Figure 2. Absorption and VCD spectra of Δ- and Λ-Co(acac)₂(L-alaninato) in CDCl₃ solution in the hydrogen stretching region. The concentrations and path lengths for the Δ and Λ complexes were 0.036 M at 750 μm and 0.037 M at 750 μm, respectively.

measurements in the aliphatic CH stretching region, as well as in the mid-infrared region, with this solvent. The spectra in Figure 2 can be assigned easily as the antisymmetric NH_2 stretching mode at higher frequency and the corresponding symmetric mode at lower frequency as provided in Table II. Not shown in Figure 2 is a weak band in both complexes at 3090 cm⁻¹ assigned to the acac methine CH stretching mode which shows no observable VCD intensity. Both the absorption and VCD spectra of the NH modes exhibit the same relative features as the spectra obtained from Me_2SO-d_6 solution. Namely, the absorption bands of the Δ complex are slightly broadened and shifted to lower frequency and have lower peak intensities in comparison to those of the Λ complex. The VCD spectra for the two complexes have the same relative intensities, but those of the Δ complex are significantly more intense than those of the Λ complex, although the discrepancy is not as large as that encountered in Me_2SO-d_6 solution.

In spite of the similarities in the interpretation and relative features of the VCD spectra in Me_2SO and CDCl₃, significant differences are present in the observed frequencies and intensities of the absorption spectra. The bands in CDCl₃ are clearly less affected by hydrogen bonding; they are narrower and occur at a higher frequency. Most likely the two NH bonds are more equivalent in CDCl₃; their splitting of ~60 cm⁻¹ is characteristic of vibrational splitting into pure symmetric and antisymmetric modes. The much larger splitting in Me_2SO is indicative of somewhat inequivalent NH bonds where presumably one bond is more strongly hydrogen bonded to the solvent than the other. The differences is absolute and relative intensity can also be attributed to hydrogen bonding interactions of different strengths in the two solvents.

Mid-Infrared Spectra. In Figure 3 are presented the Fourier transform infrared absorption and VCD spectra for the Δ and the Λ complexes of Co(acac)₂(L-alaninato) in Me_2SO-d_6 solution for the region spanning 1600 to 1180 cm⁻¹. In this region the two
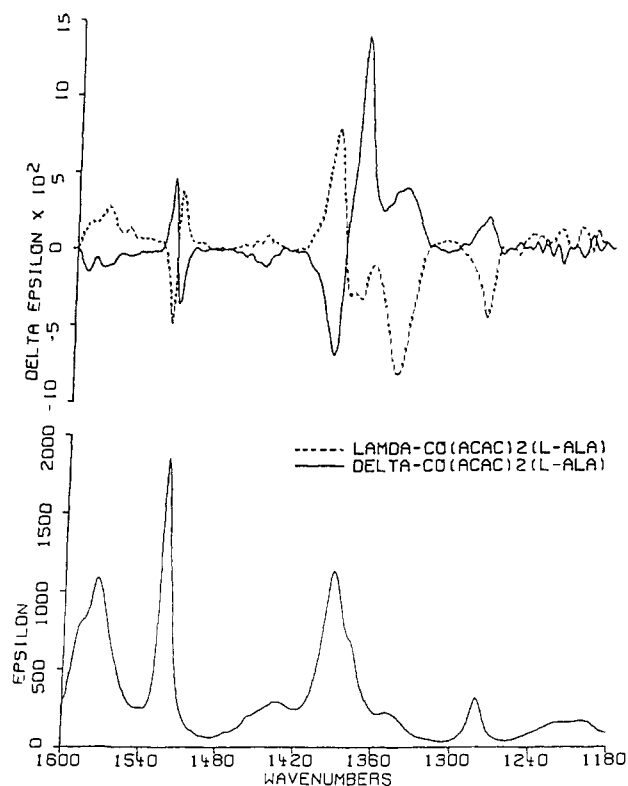
Figure 3. Fourier transform absorption and VCD spectra of Δ- and Λ-Co(acac)₂(L-alaninato) in Me_2SO-d_6 solution in the mid-infrared region. The concentration and path length for both complexes were 0.07 M and 50 μm.
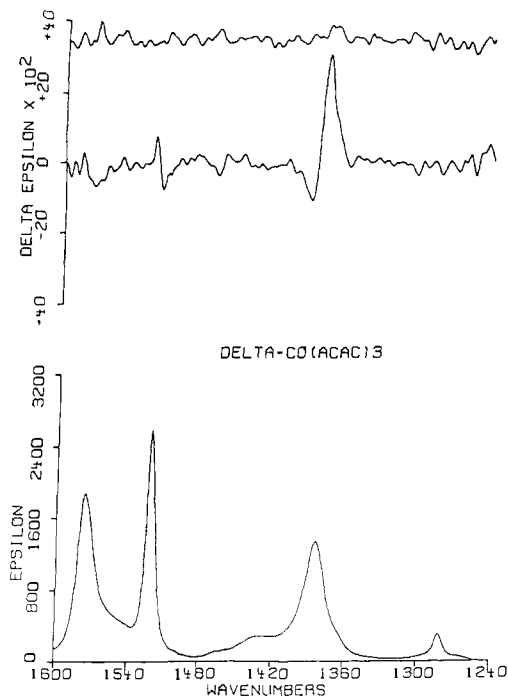

Figure 4. Fourier transform absorption and VCD spectra of Δ-Co(acac)₃ in Me_2SO-d_6 solution in the mid-infrared region. The upper-most trace is an estimate of the instrumental noise for the VCD spectrum. The concentration and path length were 0.028 M and 50 μm.

diastereomers have effectively the same absorption spectra and hence only one absorption curve is presented. The corresponding band frequencies, intensities, and mode assignments are provided in Table I. For comparison, the FT–IR and FT–VCD spectra of Δ-Co(acac)₃ in Me_2SO-d_6 solution are displayed in Figure 4 with frequencies, intensities, and assignments listed in Table III.

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Table III. Frequencies (cm^{-1}), Intensities (cm^{-1} L mol^{-1}), and Assignments for the Absorption and VCD Spectra of Λ-Co(acac)$_3$ in Me$_2$SO-d_6 Solution

absorption spectra		VCD spectra		
frequency	intensity	frequency	intensity × 10^3	assignment
1576	1800	1576	−50	ν^a_{CO}
1521	2600	1524	+80	ν^a_{CC}
		1519	−80	
1431	300			$\delta^a_{CH_3}$
1385	1350	1394	−100	ν^s_{CO}
		1380	+320	
1366	400			$\delta^s_{CH_3}$
1281	300			δ_{CH}

Assignments of the vibrational frequencies of acac modes in the mid-infrared region have been reported previously.[24,26] Similarly, the vibrational modes of alanine in this region have been described on several occasions.[27,28]

The pair of absorption bands at 1585 and 1576 cm^{-1} in the alaninato complex and 1576 cm^{-1} in the tris(acac) complex are assigned to the antisymmetric CO stretch of the acac ligand. The appearance of two bands in the alaninato complex is attributed to the inequivalence of its two acac ligands, i.e., one acac has a CO group trans to the alaninato amino group while the other has a CO group trans to the alaninato carboxylic acid group. The narrow, intense absorption band at 1522 cm^{-1} in both complexes is assigned to the antisymmetric CC stretching mode of the acac ligand. There is no change in these bands upon deuteration, indicating further that intensity due to the NH scissors mode is not present below 1600 cm^{-1}. The band features in the 1460 to 1420 cm^{-1} region are assigned to antisymmetric methyl deformation modes. The band at 1385 cm^{-1} in the tris(acac) complex is due to the CO symmetric stretching mode. In the alaninato complexes this band appears at 1390 cm^{-1} and also contains the symmetric CO$_2^-$ stretching mode. The symmetric methyl deformation mode appears as a weak shoulder at 1366 cm^{-1} in the tris(acac) complex and at 1378 cm^{-1} in the alaninato complex. The only remaining assignable feature in the tris complex is the methine CH bending mode at 1281 cm^{-1}, whereas the alaninato complex possesses two additional modes at 1348 and 1282 cm^{-1} due to the methine CH bending modes of the alaninato ligand.

The VCD spectrum of the Δ-tris(acac) complex exhibits negative intensity in the antisymmetric CO stretching region and a positive–negative (higher to lower frequency) couplet in the antisymmetric CC stretching band. The largest VCD feature appears in the region of the symmetric CO stretching mode as a negative–positive couplet biased heavily to positive intensity. Other features cannot be discerned above the level of the noise, which was higher than that encountered in the alaninato complex due to the incomplete optical resolution of the tris(acac) complex as noted in the Experimental Section.

The VCD spectra of the Δ- and Λ-alaninato complexes are very close to enantiomeric in the 1600 to 1400 cm^{-1} region where contributions from the acac ligands dominate and then deviate from a mirror image relationship below 1400 cm^{-1} as large contributions from the alaninato ligand enter. Unlike the hydrogen stretching region, at no point do the two complexes exhibit the same VCD bands, indicating that isolated alaninato contributions are not present. The Δ-alaninato complex possesses qualitatively the same VCD features in the three strongest absorption band regions as those observed in the Δ-tris(acac) complex, providing further evidence for the origin of these features to be the acac ligands.

VCD Spectral Interpretation

The VCD spectra in the hydrogen stretching region displayed in Figures 1 and 2 have their origin in the alaninato ligand. Since
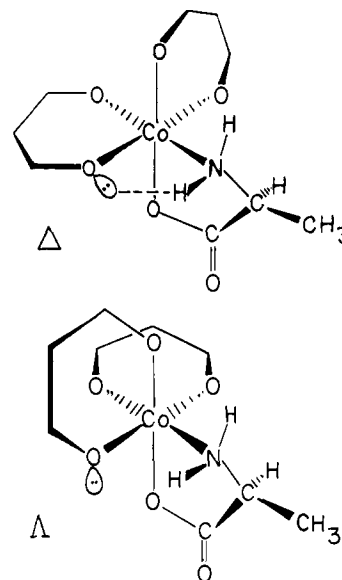
Figure 5. Stereodiagrams of Δ- and Λ-Co(acac)$_2$(L-alaninato) showing the formation of an intramolecular hydrogen bond in the Δ complex.

the acac ligand is planar and inherently achiral, it cannot be a source of optical activity without coupling to adjacent ligands. Coupling in these two diastereomeric complexes would lead to opposite VCD for the complexes, which is not observed. The simplest explanation for the observed VCD is that the band for both complexes at 2930 cm^{-1} is due to the methine CH stretch of the L-alaninato ligand which induces a ring current in the chelate ring, as concluded in previous investigations of amino acid–transition-metal complexes. The spectra in the NH stretching region must involve some chiral configuration of the alaninato NH$_2$ group that produces the same VCD effect in both complexes, but with a major enhancement for the Δ complex.

Stereodiagrams of the Δ complex and the Λ complex are shown in Figure 5. In both complexes the conformation of the L-alaninato ligand puckers in a manner that causes the NH$_2$ group to assume the orientation depicted. The pucker of the L-alaninato ligand, although not as severe as that of the ethylenediamine ligand, has been shown to place the methyl group of the alaninato ligand in an equatorial conformation relative to the alaninato chelate ring.[29,30] According to this argument, the D-alaninato ligand puckers in the opposite direction. With the NH$_2$ group in the orientation shown, an intramolecular hydrogen bond can form in the Δ complex between one of the amino hydrogens and an oxygen on the acac ligand through an occupied lone pair orbital. In the Λ complex such a hydrogen bond will not form as favorably since in this case the σ lone pair orbital of the acac oxygen does not project toward the amino hydrogen.

The detailed description of the ring current mechanism that leads to enhanced VCD in the NH stretching modes of the Δ complex is illustrated in **1** for the symmetric stretching vibration.
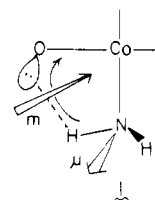
The electric dipole transition moment lies in the plane of the NH$_2$ group and is directed midway between the two NH bonds. The phase of the vibrational cycle depicted corresponds to the elongation of the NH bonds and μ points in the direction of the positive end of the dipole moment. To establish the direction of current

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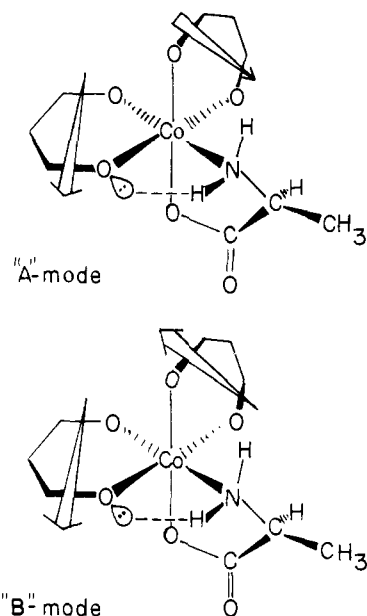
Figure 6. Stereodiagrams of the "A" and "B" modes of the in-plane CC stretching vibrations of Δ-Co(acac)$_2$(L-alaninato).

density in the ring formed by the alaninato–acac hydrogen bond, it can be noticed that for the phase of the vibrational motion in 1 the distance between the bonding amino hydrogen and the acac oxygen will be shortening. A shorter hydrogen bond is a stronger one with a greater amount of electron density in the bonding region. The additional electron density is supplied by the more electron rich member of the hydrogen bonding pair, namely the acac oxygen, and this establishes the direction of the current. The curved arrow in the diagram indicates the direction of positive current flow in the intramolecular ring, and by the right hand rule of current moving in a arc or loop the direction of the magnetic moment, **m**, is determined. Finally, the rotational strength, R, is obtained as the projection of the vector μ on the vector **m** from the theoretical expression, where Im indicates the imaginary part.

$$R = \text{Im}(\mu \cdot \mathbf{m}) \qquad (1)$$

Since μ and **m** point in opposite directions, the predicted VCD intensity from this mechanism is negative. The arguments for the observed positive VCD intensity in the antisymmetric NH$_2$ stretching region are the same as those given above for the symmetric stretching mode except that the phase of the amino hydrogen that is not hydrogen bonded is reversed; the ring current and magnetic dipole are in the same direction, but the electric dipole moment points into, rather than out of, the plane of the ring and μ and **m** have a positive vector overlap.

As discussed in the Results section, the mid-infrared region is dominated by coupled acac vibrational modes. Since the stereochemistry for the Δ- and Λ-alaninato complexes is opposite with respect to the acac ligands, it follows that VCD effects dominated by acac transitions will be opposite in nature. While the VCD spectra below 1400 cm^{-1} show combined effects of both acac transitions and L-alaninato transitions, the CC antisymmetric in-plane stretching mode at 1522 cm^{-1} is a pure acac mode that exhibits nearly equal and opposite VCD spectra. The origin of this VCD effect appears to be an interaction described by the elementary form of the coupled oscillator model. The transition moment for this vibrational mode is illustrated in 2 where it can

be seen that the moment lies in the acac plane and is perpendicular to the axis that bisects the ring and passes through the cobalt atom. The same vibrational motion on each of the two acac ligands in the complex couple to yield a pseudo-A mode and a pseud-B mode that are split in frequency and have equal and opposite VCD intensities. The designations pseudo-A and -B enter by initially regarding the complex as having C_2 symmetry but recognizing that the alaninato ligand, as a remote influence, lowers the symmetry to the C_1 point group. The phasing of the two near-degenerate vibrational modes is depicted in Figure 6.

The observed VCD couplet at 1522 cm^{-1} in Figure 3 is the residual of the oppositely signed VCD from these two modes which would completely cancel were it not for the presence of frequency splitting. The corresponding VCD couplet in the tris(acac) complex is produced by a threefold coupling of the acac ligands to form an A mode having one sense of VCD intensity and a degenerate E mode having the opposite VCD intensity. Again, a frequency shift is present that is opposite for the modes of different symmetry and gives rise to the observation of a bisignate VCD spectrum.

As a final point we comment on the nature of the large couplet centered at 1386 cm^{-1} with extrema at 1396 and 1377 cm^{-1}. The parent absorption band at 1390 cm^{-1} with a shoulder at 1378 cm^{-1} is assigned in Table I to four kinds of modes, symmetric CO stretching modes of the acac and ala ligands and symmetric CH$_3$ deformations (umbrella modes) of both ligands. While the bisignate nature of the VCD most likely originates in the coupled oscillator mechanism for the acac CO stretching modes, a detailed interpretation is prevented by a lack of precise knowledge regarding the orientation of the relevant electric dipole transition moments in the acac rings. The possibility of strong coupling of the acac CO stretching mode with the ala CO stretching mode, as well as with the acac CH$_3$ deformation modes, is responsible for this uncertainty. A related problem is whether the electric dipole moment of the CO symmetric stretch should be modeled as one moment per acac ring or two moments (one along each CO bond) per ring. In the former case, no VCD is obtained to zeroth order whereas in the latter case a net VCD couplet may appear.

Model Calculations

Coupled Oscillator Calculation. A general formulation of the coupled oscillator model of circular dichroism for a pair of electric dipole oscillators at arbitrary angles of orientation with respect to one another has been described by Tinoco.[31] With use of the angular conventions provided in Tinoco's paper, the orientations of the two acac transition dipoles for the pseudo-B mode ("B" mode) of the Δ complex at 1522 cm^{-1} are shown in Figure 7. Assuming these two dipoles to be equivalent, their magnitude, μ, can be obtained from the measured dipole strength, D, of the
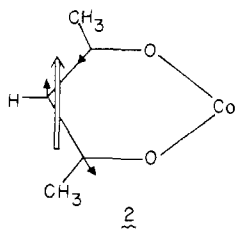

Figure 7. Orientations of the two electric dipole moments of the in-plane "A" mode for the acac antisymmetric CC stretching vibration. The values of the angles are $\theta_1 = 90°$, $\phi_1 = 73°$, $\theta_2 = 18°$, $\phi_2 = 58°$.

(31) Tinoco, I. *Radiat. Res.* **1963**, *20*, 133.

Table IV. Calculated and Observed Intensity Parameters for the Coupled Oscillator Calculation of the 1522-cm^{-1} Band in Δ-Co^{III}(acac)$_2$(L-alaninato)

mode	D(calcd) × 10^{38} (esu cm)^2	R(calcd) × 10^{42} (esu cm)^2	$\Delta\epsilon$(calcd) (cm^{-1} L mol^{-1})	$\Delta\epsilon$(obsd) (cm^{-1} L mol^{-1})	$\Delta\bar{\nu}$(calcd) (cm^{-1})
"B"	8.44^a	+7.79	+0.038	+0.045	0.32
"A"	4.56^a	-7.79	-0.038	-0.038	-0.32

^{a} The sum of the dipole strengths for the "A" and "B" modes is the observed dipole strength 1.30 × 10^{-37} esu^2 cm^2 obtained from $D = 0.92 \times 10^{-38} \int \epsilon/\nu \, d\nu$. The entries in the table are given by $D_B = \mu^2[1 + \sin\theta_2 \cos(\varphi_1 - \varphi_2)]$ and $D_A = \mu^2[1 - \sin\theta_2 \cos(\varphi_1 - \varphi_2)]$.

Table V. Intensities, Transition Dipoles, and Ring Currents for the Hydrogen Stretching Modes in Δ- and Λ-Co^{III}(acac)$_2$(L-alaninato)

mode	D × 10^{39} (esu cm)^2	R × 10^{44} (esu cm)^2	μ × 10^{20} (esu cm)	m × 10^{24} (esu cm)	I × 10^{-11} (e/s)	$\partial I/\partial P$ × 10^3 (e/amu$^{1/2}$ Å)
			Me$_2$SO-d_6 Solution			
Δ-$\nu^s_{NH_2}$	35.6	-59.4	18.8	4.48	6.18	14.5
Λ-$\nu^s_{NH_2}$	38.6	-3.33	19.6	0.241	0.333	0.80
Δ-, Λ-$\nu_{C_\alpha H}$	1.59^a	+7.57	3.99	1.90	1.68	4.0
			CDCl$_3$ Solution			
Δ-$\nu^a_{NH_2}$	3.84	+6.15	6.20	1.97	2.71	6.42
Δ-$\nu^s_{NH_2}$	1.81	-8.92	4.26	2.97	4.09	9.64
Λ-$\nu^a_{NH_2}$	3.80	+1.64	6.16	0.529	0.731	1.81
Λ-$\nu^s_{NH_2}$	2.19	-1.66	4.68	0.504	0.694	1.62

^{a} Estimated from the dipole strength of alanine–Cd$_3$Nd$_3$ and alanine–Nd$_3$ and the scaled observed overall dipole strength of Co^{III}(acac)$_2$(L-alaninato) in the CH stretching region.

1522-cm^{-1} band by the relation $\mu = (D/2)^{1/2}$. The expressions for the rotational strength and the frequency shift are given by

$$R = -\left(\frac{\pi\bar{\nu}_0}{2}\right) T_{12}\mu^2 \sin\phi_1 \cos\theta_2 \tag{2}$$

$$\Delta\bar{\nu} = -\left(\frac{\mu^2}{hcT_{12}{}^3}\right) \times$$
$$[\sin\theta_2 \cos(\phi_1 - \phi_2) - 3\sin\theta_1 \sin\theta_2 \cos\phi_1 \cos\phi_2] \tag{3}$$

where $\bar{\nu}_0$ is the center frequency of the absorption band, T_{12} is the distance between the centers of the transition dipoles, and ϕ_1, θ_1, ϕ_2, and θ_2 are orientation angles defined in Figure 7. The distance between the two dipoles is taken to be 5.4 Å, the distance between the central carbon atoms in the acac rings, and this distance has been obtained from the reported X-ray structure of tris(acac)Co^{III}.[32] A peak height in epsilon units that can be compared directly to experiment assuming Gaussian band shapes can be obtained by using[14d]

$$\Delta\epsilon = (7.48 \times 10^{38})\bar{\nu}_0 R(\Delta\bar{\nu})\pi^{-1/2}\Delta^{-2} \tag{4}$$

where Δ is the half-width of the absorption band at a height of 1/e of the band maximum; in this case, it is 6.5 cm^{-1}. The calculated and observed values for the "A" and "B" modes are also given in Table IV. Comparison of these values is quite favorable. Agreement in sign is achieved by the positive intensity of the "B" mode, calculated to have a positive frequency shift, and negative intensity in the "A" mode, predicted to shift to lower frequency. A positive–negative couplet (as defined above) is both calculated and observed. Since the observed and calculated peak intensities are also very close, one concludes that no other major intensity source needs to be invoked to explain the observed data.

Ring Current Calculations. The VCD features in the hydrogen stretching region have been interpreted in terms of vibrationally generated ring currents. In this section we perform a simple analysis of these spectra to determine values of electronic current that need be present in these intramolecular rings in order to generate the observed VCD by this mechanism. To do this we first present the elements of a model of VCD intensity that we refer to as the vibrational ring current model. A more complete exposition of this model will be given elsewhere.[33]

We first assume that the ring current does not contribute to the electric dipole transition moment. This is essentially an assumption that the current occurs in the ring with no redistribution

of electronic charge. Any buildup of charge at points around the ring would produce an electric dipole moment contribution; however, a ring current at constant electron density throughout the ring gives rise to a pure magnetic dipole moment without an electric dipole component.

The next step is to determine the direction and magnitude of the inducing electric dipole transition moment. The direction is obtained from the trajectories of the stretching motion and the magnitude is obtained from the square root of the observed dipole strength, namely

$$\mu = (D)^{1/2} \tag{5}$$

We next assume that the current in the intramolecular ring travels in a planar circular path. The current generates a magnetic dipole transition moment, **m**, that is normal to the plane. If θ is the angle between the directions of the vectors μ and **m**, we can calculate the magnitude of the magnetic moment from

$$m = \frac{R}{\mu \cos\theta} \tag{6}$$

where R is the rotational strength of the observed VCD band. From electromagnetic theory, the relationship between a magnetic moment generated by a current, I, in a closed circular loop is given by[34]

$$m = \frac{\pi a^2}{c}I \tag{7}$$

where a is the radius of the closed loop and c is the speed of light. By using eq 5 through 7, the desired values of ring currents can be calculated. These values along with other intensity parameters are listed in Table V. The only exception is the antisymmetric NH$_2$ stretching mode for Co(acac)$_2$(L-alananato) in Me$_2$SO-d_6 solution where the observed VCD, as described above, is thought to contain interfering contributions from a Fermi enhanced overtone band. The ring current calculations for the CH stretching mode are the same for both the Δ and Λ complexes. The radius of the ring involving the NH stretching modes was estimated to be 1.2 Å based on the bond lengths and bond angles of the four-membered ring, **1**. Values for the length of the Co–O(acac) bond (1.898 Å) and the Co–N bond (1.945 Å) were obtained from the literature for the tris(acac)Co^{III} complex[32] and the (–)-*mer*-Co(L-ala)$_3$ complex,[35] respectively. The radius of the five-membered ring associated with the C$_\alpha$H mode was estimated to be 1.5

(32) Hon, P. K.; Pfluger, C. E. *J. Coord. Chem.* **1973**, *3*, 67.
(33) Nafie, L. A.; Freedman, T. B., submitted for publication.

(34) Jackson, D. "Classical Electrodynamics"; Wiley: New York, 1962; p 147.
(35) Herak, R.; Prelesnik, B.; Krstanovic, I. *Acta Crystallogr.* **1978**, *B34*, 91.

Å. The angle θ between μ and $\mathbf{m}$ for the NH stretching modes was determined to be 44.8°, whereas 0° was assumed for θ in the case of the C_aH stretching mode. For the NH stretching modes it was assumed that the NH group involved in the hydrogen bond to the acac oxygen is contained in the plane of the other three atoms of the intramolecular ring. Owing to the number of simplifying assumptions in these calculations, only qualitative estimates of the value of the currents are expected.

A general result of the ring current calculations is that the magnitude of the current in the Δ complexes for the NH stretching modes is within nearly a factor of 2 for the three vibrational modes (two solvents) calculated, in spite of a much greater variation, approximately an order of magnitude, in the rotational strength. Further, the ring current of the Δ complex is more than an order of magnitude larger than the corresponding current in the Λ complex in Me_2SO-d_6 solution and somewhat less than an order of magnitude larger in $CDCl_3$ solution.

A final quantity in Table V is the transition ring current obtained as the derivative of the current with respect to the conjugate momentum of the normal coordinate of vibration, $(\partial I / \partial P)$. In the formulation of VCD in the charge flow[5] and nonlocalized molecular orbital[6] models, use is made of the relationship between the charge flux at an atomic center, $\partial \rho / \partial Q$, and the sum of charge flows (currents), $\partial I / \partial P$, in bonds associated with that atomic center. In these models, values for the charge flows have been calculated which may, in principle, be compared in magnitude to the values of $\partial I / \partial P$ listed in Table V. It should be noted, however, that these models have no provision for calculating net charge flows around a molecular ring. If a ring is present, the net charge is usually assumed to be zero. The values of $\partial I / \partial P$ in Table V have been obtained by using the relation

$$I = (\partial I / \partial P) \langle P \rangle_{10} \qquad (8)$$

where $\langle P \rangle_{10}$ is the vibrational transition matrix element of the momentum operator for a fundamental transition and is equal to $(\hbar \Omega / 2)^{1/2}$, in the harmonic approximation, with Ω representing 2π times the vibrational frequency. Although values of charge in Table V for $\partial I / \partial P$ are not large ($\sim 10^{-2}$ e), they do represent a source of magnetic dipole strength that is unopposed by the motion of nuclei having opposite charge and, therefore, are influential in generating large VCD effects.

Discussion

The example of the coupled oscillator at 1522 cm^{-1} in these complexes represents one of clearest instances of this elementary mechanism of VCD intensity. It is also the first report of the occurrence of the coupled oscillator mechanism of VCD in a transition-metal complex. By comparison to previous examples of the coupled oscillator,[14] the parent band is approximately a factor of 2 narrower and the frequency shift of the modes, at only 0.32 cm^{-1}, is quite small. Typically, shifts of 1 cm^{-1} or more are encountered. The small frequency shift is due to the near orthogonal orientation of the two coupling transition moments, cf. Figures 6 and 7. Since the shift is approximately an order of magnitude smaller than the bandwidth, it follows that a similar reduction in the observed peak heights, compared with the intrinsic peak heights, is present. From Tables I and IV it can be ascertained that the anisotropy factor of the observed VCD couplet, measured from positive to negative peak height divided by the peak absorption intensity, is 4.6×10^{-5} whereas the value of the corresponding theoretical quantity, obtained from $(4R/D)$, is 4.8 $\times 10^{-4}$. The magnitude of the rotational strength for each member of the couplet, 7.79×10^{-42} esu^2 cm^2, is also the largest rotational strength determined to date for the coupled oscillator effect in a vibrational transition. This large value arises for the same reason as the small frequency splitting, namely, the near orthogonal orientation of the two oscillators.

It is gratifying that such close agreement is found between the calculated and observed values of the peak intensities. The purity of the vibrational transitions, the absence of significant overlap with interfering transitions, and the high signal-to-noise ratio are all contributing factors to the level of agreement achieved. With

this example, there should be little remaining doubt concerning the isolated occurrence of the coupled oscillator mechanism for circular dichroism in vibrational transitions. The only discrepancy in the present example is the presence of a slight imbalance in the magnitude of the high and low frequency members of the couplet which cannot be accounted for within the coupled oscillator formalism. This bias (positive for the Δ complex) most likely arises from the influence of the intrinsically chiral alaninato ligand.

The example of the ring current mechanism of VCD intensity represents the most conclusive single occurrence of this effect to date. The salient feature of the evidence in Figure 1 is the dramatic difference in VCD *intensity* for the NH stretching bands of the Δ complex vs. the Λ complex with very little difference in the absorption spectra. These results are consistent with the presence of a large ring current in the Δ complex that is not present in the Λ complex. The ring current, which can be present without alteration of the electron density distribution of the molecule by virtue of its cyclic nature, does not contribute to the absorption spectrum but does contribute heavily to the magnitude of the VCD spectrum.

The slight diminishment of absorption intensity, as well as the slight broadening of the bands, in the Δ complex can be understood in terms of the formation of an intramolecular hydrogen bond. The loss of intensity is most likely due to the formation of a pathway for the passage of electronic charge that would otherwise accumulate at or be depleted from the end of the NH bond. The increased bandwidth is simply due to the added perturbation to the hydrogen bonding NH oscillator through the formation of the hydrogen bond.

It is interesting to consider the differences in the NH stretching VCD of these complexes in Me_2SO-d_6 and $CDCl_3$ solutions. First, it is clear that Me_2SO-d_6 interacts much more strongly with the amine hydrogens than does $CDCl_3$, decreasing the frequency of the NH stretching bands, as well as greatly increasing their bandwidth. Nevertheless, the VCD evidence in light of the ring current mechanism points to the possibility of a specific solvent interaction between the complexes and $CDCl_3$. Since the difference in VCD intensities for the Δ and Λ complexes is not as great in $CDCl_3$, and since the ring current decreases in the Δ complex and increases in the Λ complex upon changing solvents from Me_2SO-d_6 to $CDCl_3$, it appears that $CDCl_3$ may both interfere with the large intramolecular ring current in the Δ complex and increase it marginally from a very low value in the Λ complex. Both of these effects could be accomplished if a single $CDCl_3$ molecule formed a bridging interaction in these complexes whereby deuterium formed a weak bonding interaction with the lone pair of the acac oxygen and chlorine interacted similarly with the amino hydrogen that undergoes hydrogen bonding. Such a bridging interaction would form, if perhaps only transiently, an alternative pathway for electronic current in an enlarged bimolecular ring that would be less efficient in the Δ complex and more efficient in the Λ complex. One component of such a chloroform bridge, the bonding of the chloroform deuterium to the acac oxygen, has been reported.[36] For Me_2SO-d_6 such a bridging interaction would not be as probable due to the increased size of the pathway through the molecule as well as the poorer hydrogen bonding characteristics of methyl deuteriums vs. the chloroform deuterium. While the bridging role of $CDCl_3$ must be regarded as speculative at this point, it is interesting that VCD might be sensitive to such interactions between solute and solvent molecules.

Conclusion

The VCD spectra of $Co(acac)_2(L$-alaninato$)$ presented in this paper provide the opportunity to analyze in depth two of the most elementary mechanisms for the generation of VCD intensity, the coupled oscillator mechanism and the recently formulated vibrational ring current mechanism. The antisymmetric CC stretching vibration of the acac rings provides the basis for a graphic occurrence of the coupled oscillator effect which is in excellent agreement with theoretical calculations based on this

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intensity mechanism. The direct sensitivity of VCD to the absolute stereochemistry of the acac rings around the cobalt center is demonstrated. The NH stretching vibrations of the alaninato ligand in differing intramolecular hydrogen bonding environments with respect to an adjacent acac ligand yield a set of VCD spectra that dramatically portray the presence of a vibrationally generated ring current in the Δ- but not the Λ-complex. Sensitivity of VCD to the formation of intramolecular hydrogen bonded rings in molecules is demonstrated. Calculated ring current parameters allow comparison of the strength of this effect in different normal modes in differing environments. These data will provide a basis

for theoretical calculations of vibrational ring currents in molecules.

Registry No. Δ-Bis(acetylacetonato)(L-alaninato)cobalt(III), 39670-35-4; Λ-bis(acetylacetonato)(L-alaninato)cobalt(III), 39670-34-3.

Enhanced Vibrational Circular Dichroism via Vibrationally Generated Electronic Ring Currents

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Abstract: The enhanced vibrational circular dichroism (VCD) observed for some CH and OH stretching vibrations is interpreted in terms of a vibrationally generated electronic ring current mechanism. The molecules investigated include phenylethane derivatives, α-hydroxy acids and esters, and amino acids. The large methine CH stretching VCD in molecules containing an adjacent ring closed by hydrogen bonding or π–π interaction is not observed in molecules where these rings do not form. For the closed ring, an oscillating magnetic moment can arise from oscillating electronic ring current produced by the methine vibration and is responsible for the large VCD. Enhancement of methyl stretching VCD when through-space interaction between the methyl group and π orbitals is present and enhancement of OH stretching VCD for a hydroxyl group involved in an intramolecular ring provide further examples of vibrationally generated ring currents in VCD. General rules governing the sense of electronic current flow for a given phase of the nuclear motion are proposed which are consistent with all the spectra thus far obtained.

Vibrational circular dichroism[1] (VCD) results from two types of charge displacement occurring simultaneously during infrared excitation of a vibrational mode: linear oscillation of charge producing a nonzero electric dipole transition moment, and angular or circular oscillation of charge producing a nonzero magnetic dipole transition moment. For vibrational modes which involve the strongly coupled motion of chirally disposed oscillators, the magnetic contributions are adequately described by considering only nuclear motion with perfectly following electron density. For example, in the carbon–hydrogen stretching region, the VCD for chiral hydrocarbons arises primarily from this coupled oscillator mechanism and gives rise to conservative VCD spectra, which have no net VCD intensity over the spectral region.[2] In contrast, molecules with regions of delocalizable electron density (π bonds and lone pairs) near the oscillating nuclei often exhibit biased VCD spectra, which have a net positive or negative integrated intensity over the spectral region. In particular, we have observed that the methine $C_\alpha H$ stretching mode in L-amino acids introduces a strong positive bias in the VCD spectra in the CH stretching region for aqueous solutions at neutral pH.[3,4]

Biased VCD intensity in the hydrogen stretching regions requires angular oscillation of electronic charge density which does

not perfectly follow the nuclear motion.[5] As an explanation for the strong VCD bias in the CH stretching region in amino acids, amino acid transition metal complexes, and lactic acid, we proposed the following mechanism:[3,4] the $C_\alpha H$ stretch generates an oscillating electronic current in a molecular ring, adjacent to the methine bond, which is closed by hydrogen bonding or transition metal coordination; this oscillating ring current gives rise to a large magnetic dipole transition moment. As depicted in **1** for the $C_\alpha H$

1
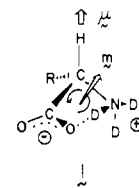
contraction in an L-amino acid, positive current, flowing in the direction $N \rightarrow C_\alpha$ when electrons are injected into the ring by the $C_\alpha H$ contraction, produces a magnetic dipole transition moment, **m**, with a component in the direction of the electric dipole transition moment, μ. The VCD intensity, represented by the rotational strength $R = \text{Im}(\mu \cdot \mathbf{m})$, is positive, as observed experimentally.

In an effort to determine whether such a mechanism can be applied more generally, we have investigated a number of molecules with a single methine $C_\alpha H$ bond and a variety of other substituents. The CH and OH stretching VCD spectra of several molecules in this class have been surveyed previously in the literature,[6-13] without complete interpretation. For this study, we

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