general quantitative utility, the present results seem to be satisfactory as a whole. Among all, what is most important seems to be the intuitiveness of the force concept, which is shown in the analyses of forces for molecular structure and chemical reactions by means of the ESE theory proposed previously.[1] The importance of the AD and EC forces is confirmed. The EGC force is less important for the cases studied here. Some important features of the electron density distribution (orbital following and preceding) in the course of nuclear displacements are also pointed out.[20,27]

Note lastly that if the density matrix P_{rs} in eq 3 is determined by some appropriate quantum-mechanical method, the computational time necessary for the calculation of force is nearly the same for any wave function. If we use wave functions which satisfy the Hellmann–Feynman theorem, the total results should be the same from both energetic and electrostatic force standpoints. However, since the latter standpoint seems to have more conceptual utility than the former, we recommend its use jointly with the former.

Acknowledgments. We acknowledge Professor T. Yonezawa for his encouraging interest in this study and Professor H. Kato and Dr. T. Kawamura for their helpful suggestions. We also thank the members of the Quantum Chemistry Group of their department for active discussions and the referees for helpful suggestions. Lastly, we wish to express our appreciation to the Data Processing Center of Kyoto University for generous use of the FACOM 230-60 computer.

Circular Dichroism of Cobalt(II) Complex between 1700 and 1200 cm^{-1}. Observation of Spin–Orbit and Tetragonal Field Splitting of the $^4T_{1g}$ Ground State Manifold

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Received May 2, 1973

Abstract: Measurements of the room temperature circular dichroism (CD) of the dimer of bis[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]cobalt reveal six bands between 1680 and 1200 cm^{-1}. The observed CD is assigned to electronic transitions of Co^{2+} from the ground and first excited Kramers doublets to the higher Kramers levels of the $^4T_{1g}$ ground manifold, which is split by spin–orbit coupling and a ligand field of tetragonal symmetry.

The circular dichroism of transition metal compounds yields valuable information on the nature of their electronic states.[1–9] Strong CD bands in the optical and near-infrared range are often used as evidence for magnetic dipole allowed transitions of the metal ion from a ground spin multiplet to excited levels of the same spin multiplicity. For systems where the major field is highly symmetric, for example, having symmetry O_h or T_d, each spin multiplet may have orbital degeneracy. Due to the spin–orbit interaction and the minor ligand field of lower symmetry, each energy level will split into sublevels. However, the observed room temperature CD of solutions usually does not reveal this sublevel structure. Indeed, even low temperature single crystal CD studies have not revealed spin–orbit splitting, as shown, for example, by Meredith and Palmer[10] for the $^3A_{2g} \rightarrow {}^3T_{1g}$ transition of Ni^{2+} in α-$NiSO_4 \cdot 6H_2O$.

An alternative method for studying this spin–orbit splitting is the measurement of CD for transitions among the sublevels of the ground state spin multiplet. The wavelength of the light inducing such transitions falls into the infrared range. This paper reports the observation of such electronic infrared circular dichroism of bis[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]cobalt measured at room temperature in CCl_4 solution between 900 and 5000 cm^{-1}.

Experimental Section

Ligand. The ligand 3-(trifluoromethylhydroxymethylene)-*d*-camphor, hereafter abbreviated tfhmc, was synthesized by the condensation of *d*-camphor with trifluoroacetyl acetonate following the method of Kopecky, *et al.*[11] The infrared absorption spectrum of a film of the ligand showed a broad band at 3350 cm^{-1} (O—H stretch), two strong peaks at 1745 and 1705 cm^{-1} (C=O stretching modes), and a relatively strong band at 1650 cm^{-1} (C=C stretch of the enol form), in addition to the bands expected from the camphor skeleton and the CF_3 group. These data agree with the ir study by Lintvedt and Fatta[12] on methylhydroxymethylene-*d*-camphor and are those expected for a β-diketone.

Complexes. Complexes of tfhmc with the ions Co^{2+}, Ni^{2+}, Cu^{2+}, and Fe^{2+} were prepared by dissolving the tfhmc in an ethanol:water mixture (7:3 v/v), adjusting the pH to 6–7, and adding to this mixture a solution of $Co(NO_3)_2$, $Ni(NO_3)_2$, $CuCl_2$, or $FeCl_2$ in the same ethanol:water solvent.[13] Evaporation of the ethanol caused precipitation of the complex. The product was filtered, redissolved

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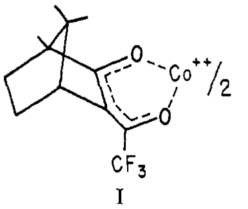
(1) W. Moffitt, *J. Chem. Phys.*, **25**, 1189 (1956).
(2) S. Sugano, *J. Chem. Phys.*, **33**, 1883 (1960).
(3) N. K. Hamer, *Mol. Phys.*, **5**, 340 (1962).
(4) T. S. Piper and A. Karipides, *Mol. Phys.*, **5**, 475 (1962).
(5) A. J. McCaffery and S. F. Mason, *Mol. Phys.*, **6**, 359 (1963).
(6) R. M. King and G. W. Everett, Jr., *Inorg. Chem.*, **10**, 1237 (1971).
(7) F. Richardson, *J. Chem. Phys.*, **54**, 2453 (1971).
(8) F. Richardson, *J. Phys. Chem.*, **75**, 692 (1971).
(9) A. D. Liehr, *J. Phys. Chem.*, **68**, 665, 3629 (1964).
(10) P. L. Meredith and R. A. Palmer, *Chem. Commun.*, 1337 (1969).
(11) K. R. Kopecky, D. Nonhebel, G. Morris, and G. S. Hammond, *J. Org. Chem.*, **27**, 1036 (1962).
(12) R. L. Lintvedt and A. M Fatta, *Inorg. Chem.*, **7**, 2489 (1968).
(13) K. J. Eisentraut and R. E. Sievers, *J. Amer. Chem. Soc.*, **87**, 5254 (1965); G. Whitesides and D. W. Lewis, *ibid.*, **92**, 6979 (1970).

in absolute ethanol, reprecipitated with water, and dried at 130° under vacuum.

The bis[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]cobalt complex is shown as structure I below and hereafter called Co(tfhmc)$_2$. The chemical composition of this complex (theoretical in parentheses) was found[14] to be C, 52.93% (52.07); H, 5.54 (5.06); Co, 9.95 (10.67). The molecular weight measured by mass spectroscopy was 553; this is consistent with the expected formula weight.



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Solutions. For circular dichroism measurement the complexs were in all cases dissolved in CCl_4. The integrity of the Co complex in this solvent was evidenced by its pinkish-brown color, by its ir absorption spectrum, and by its visible CD spectrum. In addition to absorptions of the bornane and CF_3 groups, the ir absorption spectrum showed strong bands at 1650 and 1530 cm^{-1} (overlaid by a solvent band) and a sharp band at 1300 cm^{-1} but no absorption between 1680 and 1800 cm^{-1}, as expected[12] for a metal-β-diketone complex. Lintvedt and Fatta[12] observed characteristic strong bands at 1647, 1526, and 1295 cm^{-1} for a similar hydroxymethylene-camphorato-Co^{2+} complex and assigned these bands to C=O and C=C vibrations of the ligand-metal complex. The absence of strong absorbance for $2000 > \bar{\nu} > 1700$ is evidence for the absence of free ligand in CCl_4 solvent.

The color and ir absorption of the other complexes in CCl_4 were as follows, with KBr pellet data of Lintvedt and Fatta[12] on a similar complex given in parentheses: Ni(tfhmc)$_2$ yellow green, 1655 (1644), 1520 (1516), 1295 (1301) cm^{-1}; Cu(tfhmc)$_2$ bright green, 1620 (1620), 1525 (1506), 1300 (1319); Fe(tfhmc)$_2$ dark red, 1640, 1530, and 1300 cm^{-1}. In every case the 1705- and 1745-cm^{-1} bands of the free ligand were absent.

The visible CD spectra of the complexes in CCl_4 showed the following bands: Co^{2+} 595, 535, and 495 nm; Ni^{2+} 340 nm; Cu^{2+} 390 nm; Fe^{2+} 480 and 390 nm. In addition to these bands, which must arise from placement of the metal ions in a chiral environment, CD bands were in each case observed at 310–320 nm. These presumably involve π electrons localized primarily in the ligand.[15]

Instruments. The molecular weight of Co(tfhmc)$_2$ in CCl_4 was measured using a Hitachi/Perkin-Elmer Model 115 molecular weight apparatus. The instrument was calibrated with solutions of benzil in CCl_4.

The infrared circular dichroism spectrophotometer used in our measurements has been described previously.[16] A cooled mercury-cadmium-telluride infrared detector (Texas Instruments) was employed for measurement between 900 and 2500 cm^{-1}; between 2500 and 5000 cm^{-1} a cooled InSb detector was used. The infrared CD data reported here, although of small absolute amplitude, are readily detected in our instrument. We routinely check for absorption artifacts, in the manner previously tested,[16] by measuring spectra on the instrument with the sample between the polarizer and the modulator (ABL position in Figure 1, ref 16) as well as between modulator and detector (CD position, Figure 1, ref 16). The base-line spectra (ABL) were consistently featureless.

CD spectra between 16,000 and 23,000 cm^{-1} were measured with a Cary 6003 CD instrument. Absorption spectra in the visible and near ir were measured with a Cary 14 spectrophotometer. In the ir range, a Beckman IR-10, calibrated with polystyrene film, was employed. For all spectral measurements samples of Co(tfhmc)$_2$, or other M(tfhmc)$_2$ compounds, were dissolved in CCl_4, with concentrations ranging from 20 to 200 mg/ml. The optical path length of the sample cell ranged from 0.06 to 6 mm.

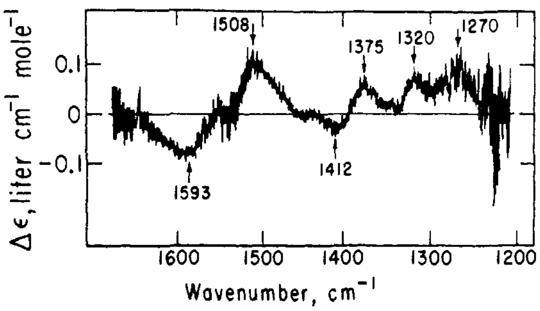

Figure 1. Circular dichroism of [Co(tfhmc)$_2$]$_2$ in CCl_4 (80 mg/ml) in the infrared, measured in a 0.09-mm cell at 300°K. The units of $\Delta\epsilon$ are l. cm^{-1} mol^{-1} of Co. The absolute accuracy of $\Delta\epsilon$ is estimated as ±25%, but the relative height of the various peaks is correct within the noise levels. The spectral slit width of the monochromator (full width at half-height) is approximately 12 cm^{-1}. We verified that the heights and widths of the bands did not change under higher resolution.

Results

Circular dichroism of Co(tfhmc)$_2$ was measured between 5000 and 900 cm^{-1}. No CD of intensity greater than $\Delta\epsilon = 0.01$ l. cm^{-1} mol^{-1} was found between 5000 and 1700 cm^{-1}. Between 1700 and 1200 cm^{-1}, however, we observed CD bands of both plus and minus sign. The intensities of the bands obey Beer's law in the concentration range we investigated (20 to 200 mg/ml). Moreover, measurements on a dried film of the compound revealed CD curves identical in shape with those found for solution. Figure 1 shows the CD spectrum measured on a solution containing 80 mg/ml of Co(tfhmc)$_2$ in a 0.09 mm path-length cell; in this range the absorption of the sample gives the best signal-to-noise ratio. The spectrum consists of two negative bands at 1593 and 1412 cm^{-1}, two positive bands at 1508 and 1375 cm^{-1}, and two overlapping bands at 1320 and 1270 cm^{-1}. The CD spectrum of this material was also examined between 900 and 1200 cm^{-1}, but no CD was observed. However, due to diminished source output and instrument throughput, the sensitivity of our instrument is reduced by a factor of 10 in this spectral range.

In order to establish whether these observed CD bands are due to electronic transitions of the Co^{2+} ions or are due to molecular vibrations, the CD of compounds Ni^{2+} (tfhmc)$_2$, Cu^{2+}(tfhmc)$_2$, and Fe^{2+}(tfhmc)$_2$ was examined. No infrared CD bands were observed for them between 5000 and 900 cm^{-1} at instrument sensitivities comparable with those of Figure 1 or stated in the previous paragraph. This observation and the observed bandwidths in the Co^{2+} complex argue strongly that the CD in Co^{2+}(tfhmc)$_2$ has an electronic origin.

The molecular weight of Co^{2+}(tfhmc)$_2$ in CCl_4 solution was measured for concentration between 10 and 40 mg/ml. We find that compound Co^{2+}(tfhmc)$_2$ is essentially a dimer in this solvent. This is not unexpected.[12,17,18] Moreover, since our CD spectra do not change with concentration, we believe that the observed CD can be assigned to a dimer [Co^{2+}(tfhmc)$_2$]$_2$.

The absorption spectrum of [Co^{2+}(tfhmc)$_2$]$_2$ in CCl_4 was also measured; the result is shown in Figure 2. A broad band can be seen centered at 8500 cm^{-1}. This must be one of the d-d transitions. The other d-d transitions in the optical range are masked by the

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[14] Elementary analyses were carried out by Galbraith Laboratories, Inc., P.O. Box 4187, Knoxville, Tenn. 37900.

[15] I. Hanazaki, F. Hanazaki, and S. Nagakura, *J. Chem. Phys.*, **50**, 265, 276 (1969).

[16] I. Chabay, E. C. Hsu, and G. Holzwarth, *Chem. Phys. Lett.* **15**, 211 (1972).

[17] D. P. Gradon, *Coord. Chem. Rev.*, **4**, 1 (1969).

[18] R. H. Holm and M. J. O'Conner, *Progr. Inorg. Chem.*, **14**, 241 (1971).

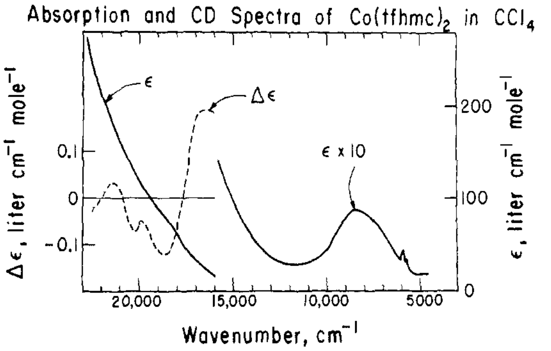

Figure 2. Visible and near-infrared absorption and CD spectra of $Co(tfhmc)_2$ in CCl_4 solution. Both ϵ and $\Delta\epsilon$ are expressed per mole of Co. The concentration of $Co(tfhmc)_2$ is 40 mg/ml.

tail of a strong band at about 30,000 cm^{-1}. In order to see the d–d transitions in this range, a CD spectrum was measured; the resultant spectrum is also shown in Figure 2. Two negative bands at 20,250 and 18,700 cm^{-1}, and one positive band at about 16,500 cm^{-1}, are found superposed on the tail of a CD band centered at energies greater than 23,000 cm^{-1}. The intensity of the latter band is affected by any small amount of water or alcohol in the solution.

Discussion

One may imagine two molecular sources for the observed infrared CD data in the Co^{2+} complex, vibrational transitions and electronic transitions. CD arising from vibrations of molecules in solution has not yet been reported, although quantitative estimates of its expected magnitude have appeared.[19-21] If changes in vibrational state of the complex generate the observed CD in the Co^{2+} complex, we would expect to see similar effects for the complexes of the other ions since their ir absorption spectra are all so similar. Moreover, we would expect some correspondence between the observed positions of the CD bands and the obvious vibrational absorption bands. Neither expectation is affirmed.

Contrariwise, if the observed infrared CD has an electronic origin, the difference between complexes of Co^{2+} and the complexes of other ions becomes understandable. One knows that the Co^{2+} ion in a octahedral field has electronic transitions in the infrared range,[22,23] whereas the Ni^{2+} and Cu^{2+} ions are not expected to exhibit electronic states between 900 and 5000 cm^{-1}. Although splitting of the $^5T_{2g}$ state of Fe^{2+} ion could[24] give an electronic transition between 800 and 1200 cm^{-1}, we observed no CD in this range or at larger wave number. To lend further support to the significance of an absence of infrared CD data in the Ni, Cu, and Fe complexes, we note that $Pr^{3+}(tfhmc)_3$, which *is* expected to have an f–f electronic transition near 2100 cm^{-1}, *does* indeed exhibit measurable CD in this region (Hsu and Holzwarth, unpublished). Finally, we suggest that the lack of correspondence between the measured infrared CD band positions and the positions of the obvious peaks in the ordinary ir absorption spectrum simply means that the parity-forbidden electronic transitions giving rise to the CD are too weak to be detected readily in the standard ir absorption curve.

The $[Co^{2+}(tfhmc)_2]_2$ complex synthesized and studied here may correspond to a mixture of stereoisomers. If only one Co^{2+} ion were involved, both cis and trans arrangements of the ligands to form a square coplanar chelate could be anticipated. For the dimer, a more complex mixture, involving at least cis–cis, cis–trans, and trans–trans assemblies, must be considered. The relationship of the two bis chelate monomers to one another is at present obscure. The groups satisfying the remaining four ligand sites are not known; presumably two are involved in a metal–metal bond.

The observed CD curve shows several peaks. Although it is possible that these correspond to the different stereoisomers, we believe a better explanation for the presence of several peaks comes from spin–orbit and tetragonal field splitting of the electronic energy levels of Co^{2+}. Such splitting could arise in a single stereoisomer. Moreover, the various stereoisomers might be expected to exhibit similar energy levels, since these are determined primarily by the MO_4 geometry in any case. Finally, as we shall see below, a sector rule which appears appropriate to the geometry of the bis chelate subunits of the complex predicts that the cis and trans stereoisomers should have CD of the same sign. Our model for the splitting is as follows.

Consider a single Co^{2+} ion in the ligand field of two tfhmc groups. The orbital degeneracy of the ^4F ground term of $3d^7$ configuration for a single Co^{2+} ion is lifted by the crystal field of the ligands. Depending upon the symmetry of the major ligand field, the ground state of Co^{2+} can be $^4T_{1g}$ in an octahedral field or $^4A_{2g}$ in a tetrahedral field. Lintvedt and Fatta[12] synthesized a cobaltous compound identical with $Co^{2+}(tfhmc)_2$ except with the trifluoromethyl group replaced by a hydrogen atom. They measured the magnetic moment of the solid phase at 300°K and found a magnetic moment of 4.9 BM for each Co^{2+}, indicating a $^4T_{1g}$ ground state for Co^{2+} ions. Our measured electronic transitions of $[Co^{2+}(tfhmc)_2]_2$ in CCl_4 indicate energy levels of Co^{2+} at 8,500, 16,500, 18,600, and 20,250 cm^{-1} above the ground level; these are very close to those of a Co^{2+} ion doped in a MgO single crystal.[25,26] In fact these energy levels are consistent with a crystal field model with a Co^{2+} ion sitting in an octahedral major field with $Dq \approx 930$ cm^{-1}. The 8500-cm^{-1} absorption band is thus assigned to the $^4T_{1g} \rightarrow {}^4T_{2g}$ and ^2E_g transitions, while the 16,500-cm^{-1} CD band is assigned to the $^4T_{1g} \rightarrow {}^4A_{2g}$ transition. The 18,700- and 20,250-cm^{-1} CD bands are assigned to the transition from $^4T_{1g}(^4F)$ to $^4T_{1g}(^4P)$ and $^2T_{1g}(^2P)$ levels, respectively, where the interaction between these two terms is large.[25,27] As noted above, the CD bands observed between 1200 and 1700 cm^{-1} must be due to electronic transitions of the Co^{2+} ions. The observed structure of the CD then presumably corresponds to splitting of the ground $^4T_{1g}$ multiplet.

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(19) C. W. Deutsche and A. Moscowitz, *J. Chem. Phys.*, **49**, 3257 (1968); **53**, 2630 (1970).

(20) G. Holzwarth and I. Chabay, *J. Chem. Phys.*, **57**, 1632 (1972).

(21) J. A. Schellman, *J. Chem. Phys.*, **58**, 2882 (1973).

(22) E. Belorizky, S. C. Ng, and T. G. Phillips, *Phys. Rev.*, **181**, 467 (1969).

(23) E. C. Hsu and J. W. Stout, *J. Chem. Phys.*, **59**, 502 (1973).

(24) J. W. Stout, M. I. Steinfeld, and M. Yazuri, *J. Appl. Phys.*, **39**, 1141 (1968).

(25) W. Low, *Phys. Rev.*, **109**, 256 (1958).

(26) R. Pappalardo, D. L. Wood, and R. C. Linares, Jr., *J. Chem. Phys.*, **35**, 2041 (1961).

(27) H. H. Marvin, *Phys. Rev.*, **47**, 521 (1935).

The intensity of a CD band for a transition from state $|a\rangle$ to state $|b\rangle$ is proportional to the rotational strength, R_{ab}, defined by[28]

$$R_{ab} = \mathrm{Im}\{\langle a|Q|b\rangle\langle b|\mathbf{m}|a\rangle\}$$

where $\mathrm{Im}\{x\}$ is the imaginary part of $\{x\}$, Q is the electric dipole operator, and $\mathbf{m}$ is the magnetic dipole operator. In order to test our hypothesis for the origin of infrared CD bands, we have performed a crystal field calculation to estimate the energy levels, magnetic transition dipole moments, electric transition dipole moments, and rotational strengths of a model complex. Now, it is known that crystal field theory gives poor results for electric transition dipole moments and rotational strengths of d–d transitions. By contrast, energy levels and magnetic transition dipole moments require fewer parameters and are more reliably obtained from this theory. We therefore present first the results of our calculations of energy levels and magnetic transition dipole moments.

The theory for the energy levels and magnetic transition moments contains a single adjustable parameter to describe the ligand field of lower symmetry. The ground $^4T_{1g}$ manifold of a single Co^{2+} is split by the spin–orbit coupling and by the ligand field of lower symmetry. The actual symmetry of the dimer $[Co^{2+}(tfhmc)_2]_2$ in CCl_4 solution is not known; however, a space-filling model built for the dimer indicates that it is reasonable to assume that the four oxygen atoms form one rectangular plane of an octahedron. The Hamiltonian, within the $^4T_{1g}$ level, of the spin–orbit coupling and a ligand field of D_{4h} symmetry can be expressed as

$$\mathcal{H} = \lambda LS + \Delta(L_z^2 - {}^2/_3)$$

where λ is the spin–orbit coupling constant (-180 cm^{-1} for a single Co^{2+} ion),[29] L and S are orbital and spin angular momentum, Δ is the tetragonal field parameter, and z is the unique axis direction. The matrix elements of the Hamiltonian, $\mathcal{H}$, and angular momentun, $L + 2S$, in the $|S,M_S,L,M_L\rangle$ representation of the $^4T_{1g}$ manifold of a Co^{2+} ion have been listed by Hsu and Stout[23,30] for the crystal field of $CoCl_2$ (D_{3d} symmetry). Within the $^4T_{1g}$ manifold a ligand field of D_{3d} symmetry is equivalent to that of D_{4h} symmetry. We have therefore used the matrix elements of Hsu and Stout in our calculation to fit the calculated energy levels to the observed CD bands. The difference of the octahedral fields in the two cases (Dq = 690 cm^{-1} in $CoCl_2$, 930 cm^{-1} in $[Co^{2+}(tfhmc)_2]_2$) is insignificant in our hypothetical model. We use Δ = 1160 cm^{-1} and λ = -180 cm^{-1} to diagonalize the Hamiltonian in $^4T_{1g}$. The eigenstates thus obtained are listed in Figure 3, together with the energy levels of a Co^{2+} ion by the successive perturbation of ligand fields. The ^4F term of a single Co^{2+} ion is split by an octahedral field into $^4T_{1g}$, $^4T_{2g}$, and $^4A_{2g}$ levels with $^4T_{1g}$ as a ground level. The $^4T_{1g}$ level is split further by a tetragonal field (D_{4h}) into $^4A_{2g}$ and ^4E_g levels. The introduction of spin–orbit coupling requires the use of the double group D_{4h}*. As expected, we find that each level is a doubly degenerate Kramers pair. It is worth mentioning here that the first excited state, at 105 cm^{-1}, is well populated at room temperature; electronic transitions from this state are therefore expected.

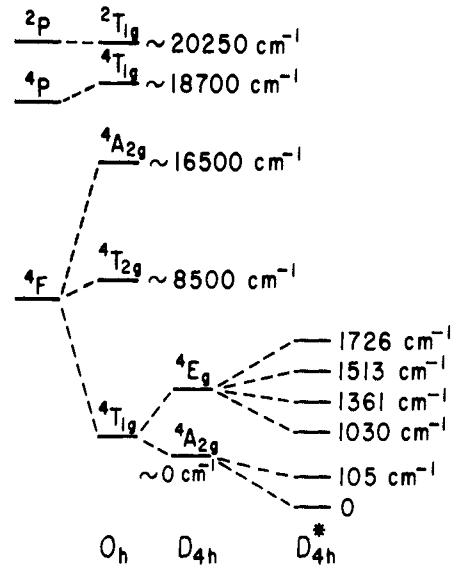

Figure 3. Energy levels of a Co^{2+} ion under an octahedral field O_h, a tetragonal field D_{4h}, and a tetragonal field with spin-orbit coupling D_{4h}*. The energies for O_h are experimental; the energies for D^*_{4h} are from theory.

The magnetic transition dipole moments between the states resulting from tetragonal field and spin-orbit splitting of the $^4T_{1g}$ level are easily evaluated. These numbers, m, summed over degenerate states and multiplied by a Boltzmann factor, are listed in Table I together with the calculated transition energies, observed transition energies, and observed rotational strengths. Although the observed rotational strengths and calculated magnetic moments are not strictly comparable, they should be correlated with one another in a rough sort of way.

Table I. Observed CD Bands and Calculated Magnetic Transition Dipole Moments of $[Co(tfhmc)_2]_2$ within the $^4T_{1g}$ Manifold[a]

Obsd		Calcd	
Energy, cm^{-1}	Rotational strength, D BM	Energy, cm^{-1}	Magnetic moment $me^{-E/kT}$, BM
		1726	0.6 × 1 = 0.6
1593	-5.2×10^{-4}	1621	5.4 × 0.6 = 3.3
1508	$+5.0 \times 10^{-4}$	1513	4.4 × 1 = 4.4
1412	-1.0×10^{-5}	1408	2.4 × 0.6 = 1.4
1375	$+2.1 \times 10^{-4}$	1361	3.0 × 1 = 3.0
1320	$\sim+2 \times 10^{-4}$		
1270	$\sim+2 \times 10^{-4}$	1255	1.2 × 0.6 = 0.7
		1030	4.2 × 1 = 4.2
		925	1.8 × 0.6 = 1.1

[a] T taken as 300°K, rotational strength $R = 2.6 \times 10^{-1} \int [\epsilon_L - \epsilon_R] d\bar{\nu}/\bar{\nu}$ with $\epsilon_L - \epsilon_R$ in l. mol^{-1} cm^{-1} and R in D BM.

The calculation predicts eight CD bands between 925 and 1726 cm^{-1}. The calculated band at 1726 cm^{-1} has a small magnetic moment and, in fact, it is not observed. The 1621-cm^{-1} band is observed at 1593 cm^{-1}; the 1513-cm^{-1} band is observed at 1508 cm^{-1}; the 1408 cm^{-1} band is observed at 1412 cm^{-1}; and the 1361-cm^{-1} band is observed at 1375 cm^{-1}. Consider-

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(28) E. U. Condon, W. Altar, and H. Eyring, *J. Chem. Phys.*, **5**, 753 (1937).

(29) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962, p 106, eq 5–36.

(30) E. C. Hsu and J. W. Stout, A.I.P.S. Document No. 02086.

ing the simplicity of our model the calculated and observed bands agree very well in their spectral positions. Moreover, the observed rotational strengths appear to correlate fairly well with the calculated magnetic dipole intensities. The observed 1320- and 1270-cm^{-1} bands, however, do not fit into this model. It is possible that the calculated energy level at 1030 cm^{-1} should be at 1320 cm^{-1}; however, we hesitate to introduce another energy parameter for such an adjustment.

We have taken our model a step further by asking whether a ligand field of odd parity, which can be expressed as a linear combination of spherical harmonics, can yield accurate electric transition dipole moments **Q** and thus explain the signs and magnitudes of the observed CD bands. The idea is to get the electric dipole transition moment for d–d transitions by a small mixing in of ungerade 4p and 4f orbitals to the gerade 3d wave functions.[1–4,8] This ungerade field should belong to the A_{1u} representation of the symmetry of the system.[3] The A_{1u} potential we used is $V_u = if(r)(Y_5^{+4} - Y_5^{-4})$, where $f(r)$ is a parameter and the spherical harmonics[31] Y_5^{-4} and Y_5^{+4} are quantized along the tetragonal axis. It has been shown by Schellman[32] and by Richardson[33] that the function $X_tY_tZ_t(X_t^2 - Y_t^2)$, where Z is the fourfold axis, has the required A_{1u} symmetry in D_{4h}. The two 1-methyl groups of the bornane structure could provide a potential of the required symmetry in either cis or trans bis complexes. Moreover, the sign of the CD would be the same for both stereoisomers. The calculated rotational strengths corresponding to the calculated magnetic transition moments in Table I were all of one sign, in contrast to our experimental results. We therefore believe that a model describing the CD signs and intensities should have wave functions which manifest the covalency between the central ion and ligands.[9] It is also possible that the interaction between two Co^{2+} ions in a molecule, which we have neglected, plays a significant role in the sign of CD bands.

It is worth speculating on the reason why we observe spin–orbit and tetragonal field structure within the $^4T_{1g}$ manifold but do not observe such structure in transitions to higher states. Although instrumental resolution may be a factor, we believe it more likely that the infrared CD measurement within the ground manifold circumvents the vibronic perturbations of the splitting of the major ligand field. These vibronic perturbations smear out the sublevel structure in transitions to higher states.

In summary, we have demonstrated that electronic transitions between sublevels of $^4T_{1g}$ in a Co^{2+} complex can be observed by infrared circular dichroism measurement at room temperature. We have also shown that the energy levels evident in the CD spectrum can be quantitatively understood in terms of a ligand field calculation. This calculation includes a major octahedral field, a minor tetragonal field, and spin–orbit interaction.

Acknowledgments. We are grateful to both the National Science Foundation for support of this research (Grant GP-8566) and to the National Institutes of Health for a research career development award to G. H. (Grant GM-15050). We thank J. Halpern for the use of apparatus for the determination of molecular weight in solution, and we thank Philip Eaton and George Temme for assistance in the synthesis of ligand tfhmc.

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(31) We follow Condon and Shortley's convention for the choice of phase for spherical harmonics: E. U. Condon and G. H. Shortley, "The Theory of Atomic Spectra," Cambridge University Press, London, 1963.

(32) J. A. Schellman, *J. Chem. Phys.*, **44**, 55 (1966).

(33) F. S. Richardson, *J. Chem. Phys.*, **54**, 2453 (1971).