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Temperature-Dependent Magnetic Circular Dichroism of Tris(diethyldithiocarbamato)chromium(III), [Cr(detc)$_3$]. Order of Spin-Forbidden [$^2T_2(t_2{}^3)$] Trigonal States and Intensity Mechanism of [$^4T_2(t_2{}^2e^1)$]

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Temperature-dependent magnetic circular dichroism (mcd) spectra are measured between ambient room temperature and 4.2°K. The data are obtained in the electronic excitation region which includes the spin-allowed transitions $^4A_2(t_2{}^3) \rightarrow {}^4T_2(t_2{}^2e^1)$ and $\rightarrow {}^4T_1(t_2{}^2e^1)$ and the spin-forbidden transition $^4A_2 \rightarrow {}^2T_2(t_2{}^3)$. At lower temperature, *e.g.*, liquid nitrogen to liquid helium, the intensity-gaining mechanism to the lower symmetry trigonal (D_3) components of the above-named states is by means of Faraday C terms due to the presence of the angular momentum in the ground state. The interpretation of the experimental mcd data for $^2T_2$, which is very intense in mcd but very uninformatively weak in electronic absorption, by means of ligand field theory including complete configuration interaction and first- and second-order spin-orbit coupling enables one to assign the order of trigonal $^2T_2$ states as $^2E > {}^2A_1$. The spin-allowed excitation to $^4T_2(t_2{}^2e^1)$ owes its very small room-temperature mcd intensity to the presence of a small amount of Faraday C activity at *ca.* 300°K. The trigonal order $^2E > {}^2A_1$ is the first $^2T_2$ assignment since ruby of the 1950's.

Introduction

We recently reported ambient room temperature mcd spectra of several trigonal chromium(III) chelates which contain the $Cr^{III}S_6$ chromophore.[2] It was pointed out that the use of mcd for these chelates is very suitable for locating d–d bands which are spin forbidden and very weak[3] in electronic absorption spectra. This advantage is especially apparent for the intraconfigurational excitation $^4A_2(t_2{}^3) \rightarrow {}^2T_2(t_2{}^3)$ because even the room-temperature mcd intensity of $^2T_2(t_2{}^3)$ is at least as great as that of the spin-allowed excitation $^4A_2(t_2{}^3) \rightarrow {}^4T_1(t_2{}^2e^1)$.[2a] The order of the trigonal states, ^2E and $^2A_1$, of $^2T_2$ was suggested but it can be determined by mcd with reliability only from (i) the knowledge of the temperature dependence of the mcd intensity and (ii) the interpretation of such intensities, or at least their signs. The basis for requirement (i) is that one must know, for example, whether the intensity of a band is primarily due to a Faraday B term or a C term,[4] so that the theoretical analysis may proceed. The low-temperature mcd measurements and a reasonably detailed analysis are given here for tris(diethyldithiocarbamato)chromium(III), [Cr(detc)$_3$], a representative of $Cr^{III}S_6$ chelates. The results have additional important consequences, since the order of a sufficient number of spin-allowed and spin-forbidden trigonal states becomes known so as to bring us to the stage where we can make a sensible choice of ligand field parameters Dq, B, C, v, and v'.

Experimental Section

The mcd apparatus was described previously,[2a] except that the JASCO wavelength cam is now accurately linear in wavelength. The sample temperature was measured with a calibrated gold–cobalt *vs.* copper thermocouple. The chelate, [Cr(detc)$_3$], was in a solid methyl methacrylate polymer matrix, prepared by dissolving a solution of CH_2Cl_2, containing the complex, in a solution of the polymer in the same solvent followed by controlled evaporation of CH_2Cl_2.

Computational Work

The analysis of the mcd structure of $^2T_2(t_2{}^2e^1)$ was carried out by computing matrix elements of the total angular momentum operator for the Faraday ratios C/D over the double-group states $\bar{E}_a$, $\bar{E}_b$, and $2\bar{A}$, or $\Gamma_4{}^a$, $\Gamma_4{}^b$, and Γ_5 and Γ_6, respectively, of Cr(III) in D_3 symmetry and with spin-orbit coupling. In order to arrive at these ratios, the weak-field procedure of the ligand field technique in the SLJM basis was employed to obtain the 120 eigenvectors of the total D_3 perturbation Hamiltonian,[5] H, or

$$\begin{aligned} H = {} & 10Dq[-{}^1\!/_5(70)^{1/2}U_0{}^4 - 2(U_3{}^4 - U_{-3}{}^4)] - \\ & \nu[{}^1\!/_7(70)^{1/2}U_0{}^2 - {}^4\!/_{21}(70)^{1/2}U_0{}^4 + {}^2\!/_3(U_3{}^4 - U_{-3}{}^4)] + \\ & \nu'[{}^4\!/_7(35)^{1/2}U_0{}^2 + {}^4\!/_7(35)^{1/2}U_0{}^4 - (2)^{1/2}(U_3{}^4 - U_{-3}{}^4)] + \\ & \zeta_d J \end{aligned}$$

J is the spin-orbit coupling perturbation, ζ_d is the one-electron spin-orbit coupling constant, U^n are the usual unit tensor operators[6] of degree n, and Dq, v, and v' have their usual meanings.[7] It is felt that v' as well as v ought to be retained in the Hamiltonian, since both the azimuthal (ϕ) and polar (θ) angles (Figure 1) of dithiocarbamate complexes differ from the octahedral values of 60 and 54.7356°, respectively.[8] The d^3 electrostatic matrices were obtained from Griffith.[9] **J** and **U** matrices were constructed by using the reduced matrix elements of Koster,[10] and the remainder of constants are evaluated with formulas given by Rotenberg, *et al.*[11] The matrix of the total angular momentum operator (only μ_z is required, $\mu_z = L_z + 2S_z$) in the SLJM basis[12] was transformed into the energy basis which includes first-order and second-order spin-orbit coupling and the full interaction of all appropriate states. These elements of μ_z are needed for the expressions of the Faraday ratios C/D (*vide infra*).

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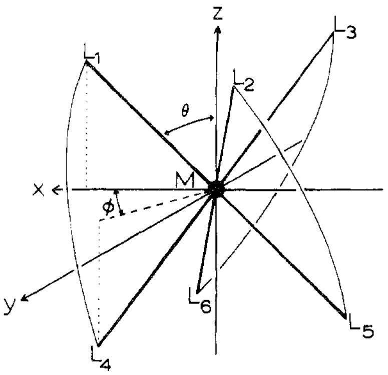

Figure 1. Azimuthal (ϕ) and polar (θ) angles of tris(bidentate) metal complexes (as part of trigonal parameter v').

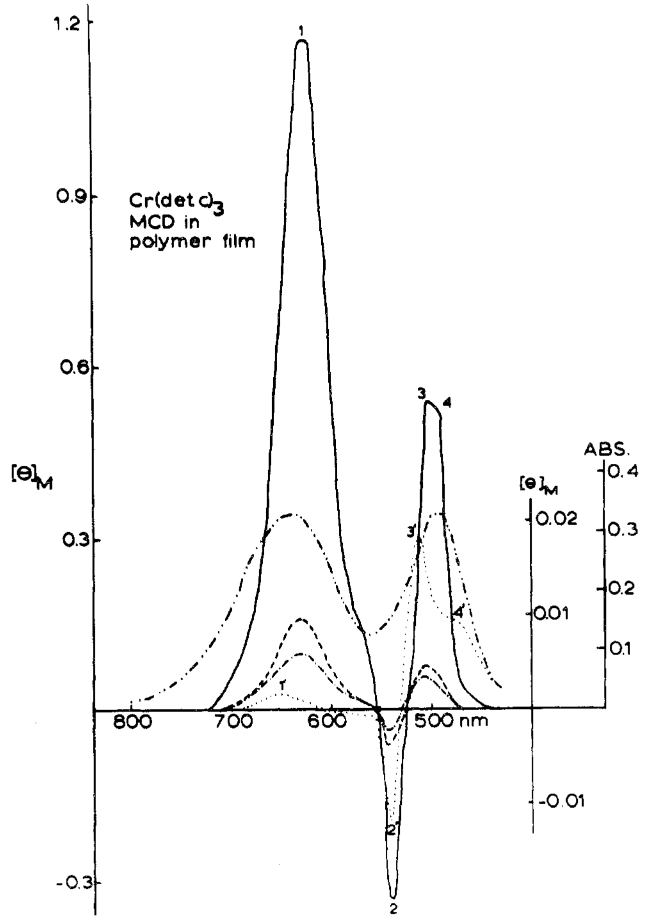

Figure 2. The temperature dependence of mcd spectra of [Cr-(detc)$_3$] in methyl methacrylate polymer film at 4.2°K (—), 60°K (- - - -), and 86°K (- · -). The left-hand scale is to be used for these spectra. The 298°K mcd solution spectrum (· · ·) and electronic absorption spectrum in polymer film (- · · · -) refer to right-hand scales.

Results and Discussion

The mcd spectra of [Cr(detc)$_3$] obtained at ambient room temperature and cryogenic temperatures are shown in Figure 2. On comparing mcd intensities at 86, 60, and 4.2°K, it is evident that all bands of ${}^4T_2(t_2{}^2e^1)$ at 630 nm, ${}^4T_1(t_2{}^2e^1)$ at 490 nm, and ${}^2T_2(t_2{}^3)$ at 506 and 546 nm (also see Figure 3) are made up largely of C terms, since for this mcd mechanism[4] the intensity is inversely proportional to the temperature

$$[\theta]_M = (\text{constant})\left[f_1\frac{C({}^4A_2 \rightarrow j)}{kT}\right]$$

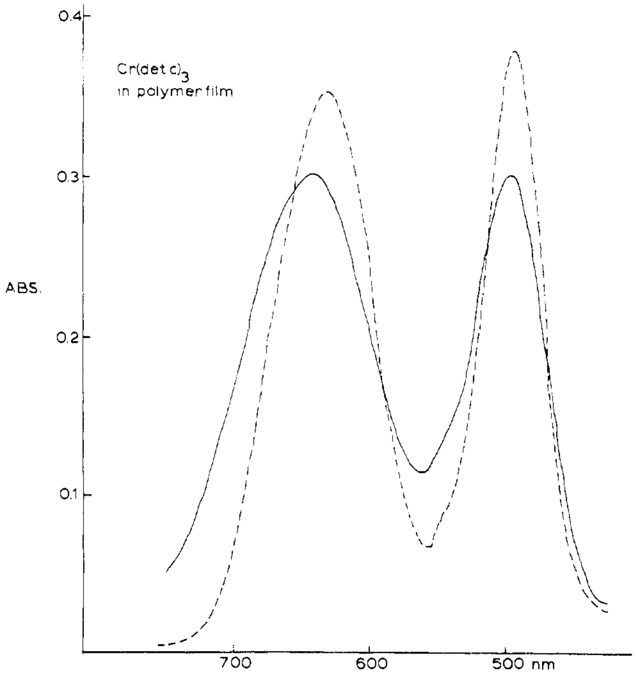

Figure 3. Electronic absorption spectra of [Cr(detc)$_3$] in methyl methacrylate polymer film at 298°K (—) and 78°K (- - -).

with f_1 the band shape function. The mcd band extrema are labeled 1 (${}^4E$, ${}^4A_1$ of ${}^4T_2$), 2 and 3 (${}^2A_1$ and ${}^2E$ of ${}^2T_2$), and 4 (${}^4E$ of ${}^4T_1$). The 4.2°K mcd spectrum is especially informative, since each band had developed fully under the conditions of these experiments. It should be noted, first of all, that the ${}^4T_2$ region (630 nm), band 1, has the largest C term activity. Second, the C term activity of ${}^2T_2$ (506-546 nm), bands 2 and 3, at 4.2°K is comparable in magnitude to, or larger than, the C term activity of ${}^4E({}^4T_1)$ near 490 nm (band 4). The other trigonal component, ${}^4A_2$, of ${}^4T_1$ is spatially forbidden in the absence of vibronic coupling, because of the D_3 selection rules

$${}^4A_2 \xleftrightarrow{x,\,y} {}^4E$$

$${}^4A_2 \xleftrightarrow{z} {}^4A_1$$

$${}^4A_2 \not\leftrightarrow {}^4A_2$$

Indeed, we find that the intensity of this electronic absorption band at about 490 nm is independent of temperature (Figure 3).

The Faraday C parameter of ${}^4T_2$ from the 4.2°K spectrum is -1.77×10^{-2} BM D^2 and the width parameter, Δ_0, is 1545 cm^{-1}. On using the room-temperature values of $\Delta_0 = 2120$ cm^{-1}, $\tilde{\nu}_0 = 15{,}625$ cm^{-1}, and the above C parameter, one predicts +0.0012 for $[\theta]_{\max}$ at room temperature (298°K). Since the experimental value of $[\theta]_{\max}$ is +0.00121, it seems that the basis for observing such low room-temperature mcd activity for ${}^4T_2$ is that the C term nearly collapses at 298°K. In contrast, the room-temperature extremes of ${}^2T_2$ remain large at room temperature because of the narrowness of the bands.

The order of trigonal components, ${}^2E > {}^2A_1$, of ${}^2T_2$ was determined in the following manner. In the first place the temperature dependence of the mcd intensity (compare θ scales for 4.2 and 298°K of Figure 2) of ${}^2T_2$ (bands 2 and 3) establishes that these two bands (506 nm) at 4.2°K are C terms of opposite sign but of comparable magnitude, even though taken together they *appear* to have the shape of an A term at room temperature.[2a,4] What remains is to show the proper association of bands 2 (positive C term, negative θ) and 3 (negative C term, positive θ) with ${}^2A_1$ and ${}^2E$ of ${}^2T_2$ by making use of the signs of C/D ratios for the ${}^2T_2$ lines. Under solution conditions

$$C(\mathrm{a} \rightarrow \mathrm{j}) = (2d_\mathrm{a})^{-1} \sum_{\mathrm{a,j},m} \langle \mathrm{a}|\hat{\mu}|\mathrm{a}\rangle \cdot \mathrm{Im}[\langle \mathrm{a}|\hat{m}|\mathrm{j}\rangle \times \langle \mathrm{j}|\hat{m}|\mathrm{a}\rangle]$$

and the dipole strength, D, is

$$D(\mathrm{a} \rightarrow \mathrm{j}) = (d_\mathrm{a})^{-1} \sum_{\mathrm{a,j},m} |\langle \mathrm{a}|\hat{m}|\mathrm{j}\rangle|^2$$

The symbols have their usual meanings, and the full expansion of the equations leads to

$$\frac{C}{D}({}^4A_2 \rightarrow {}^2A_1) = t_4{}^\mathrm{a}\langle \Gamma_4{}^+|\hat{\mu}_z|\Gamma_4{}^+\rangle$$

$$\frac{C}{D}({}^4A_2 \rightarrow {}^2E) = (t_4{}^\mathrm{b} - \frac{1}{2})\langle \Gamma_4{}^+|\hat{\mu}_z|\Gamma_4{}^+\rangle$$

where $\Gamma_4{}^+$, or $\overline{E}^+$, is a spin-orbit component of the ground state ${}^4A_2$, μ_z is the Zeeman operator, $L_z + 2S_z$, and $t_4{}^\mathrm{a}$ and $t_4{}^\mathrm{b}$ are expressions which upon evaluation would lead to positive[13] constants with values less than $+{}^1/_2$, *i.e.*

$$t_4{}^\mathrm{a} = 1/2\left(1 + \frac{M_{2\mathrm{a}}{}^2}{M_{1\mathrm{a}}{}^2}\right)$$

$$t_4{}^\mathrm{b} = 1/2\left(1 + \frac{M_{2\mathrm{b}}{}^2}{M_{1\mathrm{b}}{}^2}\right)$$

M_a and M_b are electric transition moment integrals to $\Gamma_4{}^\mathrm{a}({}^2A_1)$ and $\Gamma_4{}^\mathrm{b}({}^2E)$, respectively. For example, $M_{1\mathrm{a}} = -\langle\Gamma_4{}^+({}^4A_2)|\hat{m}_+|\Gamma_4{}^-({}^2A_1)\rangle$ and $M_{2\mathrm{a}} = \langle\Gamma_4{}^+({}^4A_2)|\hat{m}_0|\Gamma_4{}^+({}^2A_1)\rangle$, when $m_+ = (e/\sqrt{2})(y - ix)$ and $m_0 = ez$. Since the dipole strength ratios $M_2{}^2/M_1{}^2$ are positive quantities and our D_3 ligand field computation in the energy basis gives $\langle\Gamma_4{}^+({}^4A_2)|\hat{\mu}_z|\Gamma_4{}^+({}^4A_2)\rangle = +0.98$ BM, one has that C/D is positive for ${}^4A_2 \rightarrow {}^2A_1$ and C/D is negative for ${}^4A_2 \rightarrow {}^2E$. Therefore, band 2 (negative θ or positive C term) is assigned to the excitation ${}^4A_2 \rightarrow {}^2A_1$ and band 3 (positive θ or negative C term) to ${}^4A_2 \rightarrow {}^2E$. This leads to the conclusion that the energy order is ${}^2E > {}^2A_1$ for the spin-forbidden parent ${}^2T_2$. The assignment of this order of states also stands firm even if band 2 were due to $\Gamma_4{}^\mathrm{a}({}^2A_1)$ plus $\Gamma_4{}^\mathrm{b}({}^2E)$ and band 3 due to $\Gamma_{5,6}({}^2E)$, a possibility which exists in view of the signs of the C parameters for these components.

The ligand field parameters which fit the energies of the excited states ${}^4A_1(T_2)$, ${}^4E(T_2)$, ${}^2A_1(T_2)$, ${}^2E(T_2)$, and ${}^4E(T_1)$ reasonably well (Table I) are $Dq = 1560$ cm^{-1}, $B = 400$ cm^{-1}, $C = 2930$ cm^{-1}, $v = -1600$ cm^{-1}, and $v' = 315$ cm^{-1}. The sign and magnitude of v are taken from experimental results of Tomlinson's polarized crystal spectrum of Cr(dmtc)$_3$.[14] Improved computational results can be achieved by allowing the Racah C parameter to take on different values for different states.[15]

Table I. Energies of Trigonal d-d States of Cr(detc)$_3$

Band position, cm^{-1}		
Exptl	Computed	Assignment
20,280	20.264	${}^4E(T_1)$
18.380	18,380	${}^2E(T_2)$
18,210	18,220	${}^2A_1(T_2)$
15,950[a]	15,744	${}^4E(T_2)$
15,150[a]	15,077	${}^4A_1(T_2)$

[a] Band positions from Tomlinson.[14]

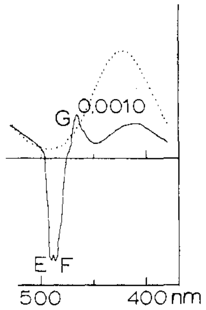

Figure 4. Solution mcd spectrum (in the ${}^2T_2$ and ${}^4T_1$ region) of $[Cr(ox)_3]^{3-}$ in water.

The analysis employed here also leads to understanding the ${}^2\Gamma_2$ structure of $[Cr(ox)_3]^{3-}$, as measured in this laboratory[2a] and elsewhere.[16] Figure 4 shows our mcd and electronic solution spectra in this region of interest, *i.e.*, ${}^2\Gamma_2$ (bands E, F, and G near 475 nm) and ${}^4T_1$ (430 nm). Taking the sharp ${}^2T_2$ mcd structure as being composed largely of C terms, then one can assign the mcd bands, E, F, and G, to excitations to $\Gamma_4{}^\mathrm{a}({}^2A_1)$, $\Gamma_4{}^\mathrm{b}({}^2E)$, and $\Gamma_{5,6}({}^2E)$, respectively. This energy order, $\Gamma_4{}^\mathrm{a} < \Gamma_4{}^\mathrm{b} < \Gamma_{5,6}$, implies ${}^2A_1 < {}^2E$, as was found for [Cr(detc)$_3$]. In fact, the room-temperature mcd spectra of $[Cr(ox)_3]^{3-}$ and [Cr(detc)$_3$] are very similar in the region of ${}^2T_2$ and ${}^4T_1$ (compare Figures 2 and 4).

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