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The determination of chiroptical dissymmetry factors and electric- *vs.* magnetic-dipole transition amplitude ratios from circularly polarized excitation and emission measurements on racemic $\mathrm{Eu(dpa)}_3^{3-}$ in aqueous solution

David H. Metcalf and F.S. Richardson
Department of Chemistry University of Virginia, Charlottesville VA 22901 (USA)

Abstract

A combination of circularly polarized excitation and emission measurements is used to determine the chiroptical properties of $\mathrm{Eu(dpa)}_3^{3-}$ complexes in aqueous solution (dpa ≡ dipicolinate dianion ≡ pyridine-2,6-dicarboxylate). Intrinsic chiroptical dissymmetry factors are measured for four absorptive and three emissive transitions, and the results are used to calculate ratios of electric- versus magnetic-dipole transition amplitudes.

1. Introduction

In neutral aqueous solution, $\mathrm{Eu(dpa)}_3^{3-}$ complexes (where dpa denotes a dipicolinate dianion) have chiral, tris-terdentate chelate structures that exist as a racemic mixture of interconverting optical isomers (enantiomers), Λ-$\mathrm{Eu(dpa)}_3^{3-}$ and Δ-$\mathrm{Eu(dpa)}_3^{3-}$. Enantiomer interconversion occurs via an intramolecular, ligand-rearrangement mechanism, and the unimolecular rate constant for Λ-$\mathrm{Eu(dpa)}_3^{3-} \leftrightarrow \Delta$-$\mathrm{Eu(dpa)}_3^{3-}$ interconversion processes is *ca.* 20 s^{-1} at room temperature [1]. Excitation of racemic $\mathrm{Eu(dpa)}_3^{3-}$ with either left- or right-circularly polarized light produces ground- and excited-state populations that are non-racemic, and luminescence from the non-racemic excited-state population exhibits chiroptical activity. That is, the luminescence contains unequal amounts of left- and right-circularly polarized emission intensity. Measurements of this chiroptical activity, as a function of excitation wavelength and emission wavelength, provide a means for characterizing the intrinsic chiroptical properties of the $\mathrm{Eu(dpa)}_3^{3-}$ complexes without having to chemically resolve and physically isolate the enantiomeric structures.

2. Experimental section

All experiments reported here were carried out on neutral aqueous solutions (at 20 °C) that contained a 20 mM concentration of $\mathrm{Eu(dpa)}_3^{3-}$. The solution samples were excited with either left- or right-circularly polarized light of variable wavelength (λ), and both the left- and right-circularly polarized intensity components of sample luminescence were measured over a range of emission wavelengths (λ'). The excitation source was a tunable dye laser pumped by a Nd:YAG laser. The linearly polarized output of the dye laser was passed through a Fresnel rhomb of 1/4-wave retardation properties to produce a circularly polarized excitation beam. All experiments were performed using pulsed excitation and time-resolved emission detection techniques. The measured quantities of principal interest were the time-integrated left- and right-circularly polarized luminescence intensities (denoted here by $\bar{I}_l$ and $\bar{I}_r$, respectively), observed as a function of emission wavelength (λ') and/or excitation wavelength (λ). The sums and differences of these quantities are generally referred to as total luminescence (TL) and circularly polarized luminescence (CPL) intensities, respectively:

$$\bar{I}(\lambda', \lambda_p) = \bar{I}_l(\lambda', \lambda_p) + \bar{I}_r(\lambda', \lambda_p) \qquad \text{(TL)} \qquad (1)$$

$$\overline{\Delta I}(\lambda', \lambda_p) = \bar{I}_l(\lambda', \lambda_p) - \bar{I}_r(\lambda', \lambda_p) \qquad \text{(CPL)} \qquad (2)$$

where the polarization state of the excitation wavelength is denoted by the subscript p (λ_+ for left and λ_- for right circularly polarized excitation). The ratio of CPL (ΔI) to TL (I) intensity is used to define the dimensionless quantity

$$\bar{g}_{\mathrm{em}}(\lambda', \lambda_p) = \frac{2\overline{\Delta I}(\lambda', \lambda_p)}{\bar{I}(\lambda', \lambda_p)} \qquad (3)$$

which is called an emission dissymmetry factor.

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3. Results and discussion

Measurements of $\overline{\Delta I}(\lambda', \lambda_p)$ as a function of λ_p (but at a fixed emission wavelength λ') yield mimics of circular dichroism (CD) spectra for Λ-Eu(dpa)$_3^{3-}$ complexes (if $p \equiv +$) and Δ-Eu(dpa)$_3^{3-}$ complexes (if $p \equiv -$). Measurements of $\overline{\Delta I}(\lambda', \lambda_p)$ as a function of λ' (using a fixed excitation wavelength λ) yield mimics of the circularly polarized luminescence (CPL) spectra of Λ-Eu(dpa)$_3^{3-}$ complexes (if $p \equiv +$) and Δ-Eu(dpa)$_3^{3-}$ complexes (if $p \equiv -$). Measurements of $\bar{g}_{\mathrm{em}}(\lambda', \lambda_p)$ emission dissymmetry factors as a function of λ' and/or λ_p can provide information about the intrinsic absorption and emission dissymmetry factors of the complexes [1,2]. The relevant relationship is [2]

$$\bar{g}_{\mathrm{em}}(\lambda', \lambda_{\pm}) = \pm 1/2\left[\frac{k_0}{k_0 + 2k_c}\right] g^{\Lambda}_{\mathrm{ab}}(\lambda) g^{\Lambda *}_{\mathrm{em}}(\lambda') \tag{4}$$

where k_0 denotes the rate constant for decay of Eu(dpa)$_3^{3-}$ luminescence, k_c denotes the rate constant for Λ-Eu(dpa)$_3^{3-} \leftrightarrow \Delta$-Eu(dpa)$_3^{3-}$ enantiomer interconversion processes, $g^{\Lambda}_{\mathrm{ab}}(\lambda)$ is an intrinsic absorption dissymmetry factor characteristic of ground-state Λ-Eu(dpa)$_3^{3-}$ complexes, and $g^{\Lambda *}_{\mathrm{em}}(\lambda')$ is an intrinsic emission dissymmetry factor characteristic of excited Λ-Eu(dpa)$_3^{3-}$ complexes. Recall from the definitions of chiroptical dissymmetry factors that $g^{\Lambda}_{\mathrm{ab}}(\lambda) = -g^{\Delta}_{\mathrm{ab}}$ and $g^{\Lambda *}_{\mathrm{em}}(\lambda') = -g^{\Delta *}_{\mathrm{em}}$ [2–6]. Under the conditions employed in the present study, $k_0 = 620\ \mathrm{s}^{-1}$, $k_c \approx 20\ \mathrm{s}^{-1}$, and eqn. (4) may be re-written as

$$\bar{g}_{\mathrm{em}}(\lambda', \lambda_{\pm}) \approx \pm 0.47 g^{\Lambda}_{\mathrm{ab}}(\lambda) g^{\Lambda *}_{\mathrm{em}}(\lambda') \tag{5}$$

Examples of $\overline{\Delta I}$ versus λ_p and $\overline{\Delta I}$ versus λ' spectra of Eu(dpa)$_3^{3-}$ complexes have been shown in several previous papers [1–3], and, due to space limitations, no spectra are shown here. Instead, we focus on results obtained from emission dissymmetry measurements carried out as a function of excitation and emission wavelength. These results are shown in Table 1. Intrinsic chiroptical dissymmetry factors are listed for four absorptive and three emissive transitions of Λ-Eu(dpa)$_3^{3-}$. The initial and final energy levels in these transitions are labelled according to their ^{2S+1}LJ multiplet parentage and their symmetry in the D_3 point group.

In the types of measurements reported here, the magnitude and sign of $g^{\Lambda}_{\mathrm{ab}}$ (or $g^{\Lambda *}_{\mathrm{em}}$) for any given transition, say $i \to j$ (or $i \leftarrow j$), are determined by the magnitudes and relative orientations of electric- and magnetic-dipole transition vectors. For the absorptive transition, $i \to j$, the relevant expression is [6]

$$g^{\Lambda}_{\mathrm{ab}}(i \to j) = \frac{4|\mathbf{P}^{\Lambda}_{ij}||\mathbf{M}^{\Lambda}_{ij}| \cos \theta^{\Lambda}_{ij}}{|\mathbf{P}^{\Lambda}_{ij}|^2 + |\mathbf{M}^{\Lambda}_{ij}|^2} = \frac{4R^{\Lambda}_{ij}}{D^{\Lambda}_{ij}} \tag{6}$$

TABLE 1. Intrinsic chiroptical dissymmetry factors and P_{ij}/M_{ij} ratios determined for $^7\mathrm{F}_{0,1} \to {}^5\mathrm{D}_{0,1}$ absorptive transitions and $^7\mathrm{F}_{1,2} \leftarrow {}^5\mathrm{D}_0$ emissive transitions of Λ-Eu(dpa)$_3^{3-}$ complexes in aqueous solution

Transition	Wavelength (nm)[a]	Dissymmetry factor		
		$g^{\Lambda}_{\mathrm{ab}}$	$g^{\Lambda *}_{\mathrm{em}}$	$\frac{P_{ij}}{M_{ij}}$
$^7\mathrm{F}_0(\mathrm{A}_1) \to {}^5\mathrm{D}_1(\mathrm{E})$	526.3	0.31		0.078[b]
$^7\mathrm{F}_0(\mathrm{A}_1) \to {}^5\mathrm{D}_1(\mathrm{A}_2)$	527.1	0.14		0.035[b]
$^7\mathrm{F}_1(\mathrm{A}_2) \leftrightarrow {}^5\mathrm{D}_0(\mathrm{A}_1)$	590.9	0.13	0.13	0.033[b]
$^7\mathrm{F}_1(\mathrm{E}) \leftrightarrow {}^5\mathrm{D}_0(\mathrm{A}_1)$	594.8	0.26	0.26	0.065[b]
$^7\mathrm{F}_2(\mathrm{E}) \leftarrow {}^5\mathrm{D}_0(\mathrm{A}_1)$	615.7		−0.06	67[c]

[a] At maximum absorption or emission intensity of the corresponding transition. The dissymmetry factors are independent of wavelength within any given transition line profile. [b] Calculated from eqn. (11). [c] Calculated from the emission analogue of eqn. (10).

where $\mathbf{P}^{\Lambda}_{ij}$ and $\mathbf{M}^{\Lambda}_{ij}$ denote electric- and magnetic-dipole transition vectors, respectively; θ^{Λ}_{ij} is the angle between $\mathbf{P}^{\Lambda}_{ij}$ and $\mathbf{M}^{\Lambda}_{ij}$; the quantity $R^{\Lambda}_{ij} = |\mathbf{P}^{\Lambda}_{ij}||\mathbf{M}^{\Lambda}_{ij}| \cos \theta^{\Lambda}_{ij}$ is defined as a transition rotatory strength; and D^{Λ}_{ij} is the total (electric plus magnetic) dipole strength of the transition $i \to j$. An analogous expression can be written for $g^{\Lambda *}_{\mathrm{em}}(i \leftarrow j)$. In axially symmetric systems, such as Eu(dpa)$_3^{3-}$, the electric- and magnetic-dipole transition vectors must be either parallel or anti-parallel (*i.e.* $\theta_{ij} = 0$ or 180°), and eqn. (6) may be evaluated to the form

$$g^{\Lambda}_{\mathrm{ab}}(i \to j) = \pm \frac{4P_{ij}M_{ij}}{(P_{ij})^2 + (M_{ij})^2} = \frac{4R^{\Lambda}_{ij}}{D_{ij}} \tag{7}$$

where the plus (+) sign corresponds to parallel transition vectors, the minus (−) sign corresponds to anti-parallel transition vectors, P_{ij} and M_{ij} represent the magnitudes (or lengths) of the transition vectors, and the superscript designation of enantiomer species (Λ or Δ) has been suppressed for all quantities that are invariant to $\Lambda \leftrightarrow \Delta$ transformations. (For Δ enantiomers, $\theta^{\Delta}_{ij} = \theta^{\Lambda}_{ij} + 180°$, and, therefore, $g^{\Delta}_{\mathrm{ab}}(i \to j) = -g^{\Lambda}_{\mathrm{em}}(i \to j)$ and $R^{\Delta}_{ij} = -R^{\Lambda}_{ij}$).

From the above discussion, it is seen that the signs of the $g^{\Lambda}_{\mathrm{ab}}$ and $g^{\Lambda *}_{\mathrm{em}}$ values listed in Table 1 provide direct information about the relative orientations of electric- and magnetic-dipole transition vectors associated with several optical absorption and emission processes in Eu(dpa)$_3^{3-}$ complexes. Additionally, the magnitudes of the measured $g^{\Lambda}_{\mathrm{ab}}$ and $g^{\Lambda *}_{\mathrm{em}}$ values can be correlated with ratios of electric- versus magnetic-dipole transition amplitudes (*i.e.* ratios of P_{ij} versus M_{ij}). For an absorptive transition ($i \to j$), this correlation is given by

$$\frac{1}{|g^{\Lambda}_{\mathrm{ab}}|} = 1/4\left[\frac{P_{ij}}{M_{ij}} + \frac{M_{ij}}{P_{ij}}\right] \tag{8}$$

and a similar expression can be written for the dissymmetry factor $|g^{A*}_{em}|$ of an emissive transition ($i \leftarrow j$). Equation (8) may be reformulated to obtain a quadratic equation of the form

$$|g^A_{ab}|r^2 - 4r + |g^A_{ab}| = 0 \qquad \left(\text{where } r = \frac{P_{ij}}{M_{ij}}\right) \tag{9}$$

If $|g^A_{ab}| = 2$ (the maximum value for a dissymmetry factor), this equation has just one solution, $r = 1$ (and, therefore, $P_{ij} = M_{ij}$). However, for any value of $|g^A_{ab}|$ less than 2, eqn. (9) has two solutions given by

$$r(P_{ij} > M_{ij}) = \frac{2 + (4 - |g^A_{ab}|^2)^{1/2}}{|g^A_{ab}|} \tag{10}$$

$$r(P_{ij} < M_{ij}) = \frac{2 - (4 - |g^A_{ab}|^2)^{1/2}}{|g^A_{ab}|} \tag{11}$$

It is known from polarized optical absorption and emission measurements on $Eu(dpa)_3^{3-}$ in hexagonal crystals of $Na_3[Yb(dpa)_3] \cdot NaClO_4 \cdot 10H_2O$ that all except one of the transitions listed in Table 1 exhibit predominantly magnetic-dipole character (*i.e.* $P_{ij} < M_{ij}$) [7]. The only exception is ${}^7F_2(E) \leftarrow {}^5D_0(A_1)$, which shows predominantly electric-dipole polarization properties. With this knowledge, one can make an informed choice between the use of either eqn. (10) or eqn. (11) in calculating P_{ij}/M_{ij} ratios from measured g^A_{ab} (or g^{A*}_{em}) dissymmetry factors. The results of these calculations are shown in the last column of Table 1. Note the decisively dominant electric-dipole character of the ${}^7F_2(E) \leftarrow {}^5D_0(A_1)$ transition, and the decisively dominant magnetic-dipole character of each of the other transitions listed.

The P_{ij}/M_{ij} ratios given in Table 1 may be used to further calculate the percentage of electric- or magnetic-dipole contribution to the total dipole strength (D_{ij}) of a transition. For the ${}^7F_2(E) \leftarrow {}^5D_0(A_1)$ transition, $100 (P_{ij})^2/D_{ij} > 99.9$ (percent electric-dipole contribution). For all of the other transitions, $100(M_{ij})^2/D_{ij} > 99.4$ (percent magnetic-dipole contribution).

4. Conclusion

This paper reports the first direct measurements of intrinsic chiroptical dissymmetry factors for enantiomeric species in a racemic mixture, and it reports the first determinations of electric- versus magnetic-dipole transition amplitude ratios based on chiroptical absorption and emission measurements.

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