

Chirality-dependent excited-state quenching of $\text{Eu}(\text{dpa})_3^{3-}$ and $\text{Tb}(\text{dpa})_3^{3+}$ luminophores by diastereomeric structures of $\Delta\text{-}[\text{Co}(\text{trans-1,2-cyclohexanediamine})_3]^{3+}$ in aqueous solution

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Abstract

Four diastereomers of $\Delta\text{-}[\text{Co}(\text{trans-1,2-cyclohexanediamine})_3]^{3+}$ are examined as enantioselective excited-state quenchers of chiral $\text{Eu}(\text{dpa})_3^{3-}$ and $\text{Tb}(\text{dpa})_3^{3-}$ luminophores (dpa \equiv dipicolinate dianion) in solution. In their quenching actions, all four diastereomers can distinguish between and interact differentially with the Λ and Δ enantiomers of the luminophores, but their enantiomeric preferences show interesting variations that may be correlated with chelate-ring conformational structure.

1. Introduction

Intermolecular chiral recognition and discrimination phenomena are of widespread interest and profound importance in chemistry and biology. In a recent series of studies, it has been shown that the chiral lanthanide complexes, $\text{Eu}(\text{dpa})_3^{3-}$ and $\text{Tb}(\text{dpa})_3^{3-}$ (where dpa denotes a dipicolinate dianion ligand), are excellent luminescent probes of chirality-dependent interactions between themselves and dissymmetric transition-metal complexes in solution [1–8]. The $\text{Ln}(\text{dpa})_3^{3-}$ complexes exist as a racemic mixture of enantiomeric structures (denoted here by ΛLn and ΔLn) in neutral aqueous solution, and excitation with a pulse of unpolarized light produces an excited-state population (ΛLn^* and ΔLn^*) which is also racemic. However, this initially racemic excited-state population (rac-Ln^*) may evolve to a non-racemic mixture of ΛLn^* and ΔLn^* enantiomers if chiral, excited-state quenching species (CQ) are present in the solution sample. The rate and extent to which the rac-Ln^* population evolves to a non-racemic mixture (with a detectable enantiomeric excess of either ΛLn^* and ΔLn^*) depend on the relative rates at which the excited states of ΛLn^* and ΔLn^* are quenched by the CQ species. The time-evolution of enantiomeric excess in the Ln^* excited-state population and the rate constants for $\Lambda\text{Ln}^*\text{-CQ}$ and $\Delta\text{Ln}^*\text{-CQ}$ quenching processes may be determined from time-resolved chiroptical luminescence (TR-CL) measurements [2–8]. Comparisons of the enantiospecific quenching constants de-

termined from these measurements (and denoted here by $k_q^{\Lambda^*}$ and $k_q^{\Delta^*}$) can provide information about both the degree and sense (handedness) of chiral discriminatory interactions between the luminophores (ΛLn^* and ΔLn^*) and quencher species (CQ).

In this paper, we report results obtained from enantiodifferential quenching studies on systems that contain either $\text{Eu}(\text{dpa})_3^{3-}$ or $\text{Tb}(\text{dpa})_3^{3-}$ complexes in aqueous (H_2O) solution with a small concentration of dissymmetric (and optically resolved) Co^{III} complexes. Cobalt(III) complexes quench $\text{Eu}(\text{dpa})_3^{3-}$ and $\text{Tb}(\text{dpa})_3^{3-}$ luminophores *via* a dynamic quenching mechanism that involves electronic energy-transfer processes in transient luminophore-quencher contact encounters [6–8]. Here we focus on a series of Co^{III} complexes that have tris-bidentate chelate structures in which three *trans*-1,2-cyclohexanediamine (*trans*-1,2-chxn) ligands are coordinated to Co^{3+} *via* amino nitrogen atoms. Each ligand has two asymmetric carbon atoms of identical absolute configuration (either *R* or *S*), and these asymmetric carbon atoms occupy the 1 and 2 (amino-substituted) positions in the cyclohexane ring. Ligands in which the absolute configuration at the asymmetric carbon atoms is *R* are denoted here by *R,R*-chxn, and those in which the absolute configuration at these sites is *S* are denoted by *S,S*-chxn. Two of the four Co^{III} complexes examined as quenchers in the present study have either all *R,R*-chxn or all *S,S*-chxn ligands, whereas the other two complexes have either 2:1 or 1:2 mixtures of *R,R*-chxn and *S,S*-chxn ligands.

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The five-membered chelate rings formed by coordination of *trans*-1,2-*chxn* to a Co^{3+} ion have rigid, non-planar conformational structures that are chiral. Chelate rings formed by *R,R*-*chxn* have a conformational chirality opposite (in handedness) to that found in chelate rings formed by *S,S*-*chxn*. Following conventions described elsewhere [9,10], the conformational chirality of *R,R*-*chxn* chelate rings is designated as λ (referring to left-handed helicity about a particular reference axis), and the conformational chirality of *S,S*-*chxn* chelate rings is designated as δ (referring to right-handed helicity about the same reference axis). Given these designations, the mixtures of chelate ring conformational chiralities in our four Co^{III} complexes are $(\lambda\lambda\lambda)$ in $[\text{Co}(\text{R,R-}i\text{chxn})_3]^{3+}$, $(\lambda\lambda\delta)$ in $[\text{Co}(\text{R,R-}i\text{chxn})_2(\text{S,S-}i\text{chxn})]^{3+}$, $(\lambda\delta\delta)$ in $[\text{Co}(\text{R,R-}i\text{chxn})(\text{S,S-}i\text{chxn})_2]^{3+}$ and $(\delta\delta\delta)$ in $[\text{Co}(\text{S,S-}i\text{chxn})_3]^{3+}$.

Each of the complexes noted above has an additional type of structural chirality defined by the helical arrangement of chelate rings around the metal atom. In the types of metal complexes considered here, this is often referred to as configurational chirality [9]. The chelate rings are viewed as forming a three-bladed propeller with either a left-handed (Λ) or right-handed (Δ) screw sense, and the configurational enantiomers are labelled accordingly as Λ and Δ . Each of the Co^{III} complexes used in the present study had Δ configurational chirality, and the complete, chirality specific notation for these complexes is given by: Δ -($\lambda\lambda\lambda$)- $[\text{Co}(\text{R,R-}i\text{chxn})_3]^{3+}$, Δ -($\lambda\lambda\delta$)- $[\text{Co}(\text{R,R-}i\text{chxn})_2(\text{S,S-}i\text{chxn})]^{3+}$, Δ -($\lambda\delta\delta$)- $[\text{Co}(\text{R,R-}i\text{chxn})(\text{S,S-}i\text{chxn})_2]^{3+}$ and Δ -($\delta\delta\delta$)- $[\text{Co}(\text{S,S-}i\text{chxn})_3]^{3+}$. Since chelate-ring conformational chirality (λ or δ) is determined entirely by ligand chirality (*R,R* or *S,S*), information about the latter is contained in the λ/δ notation, and we use the following abbreviated notation to distinguish between the four diastereomeric structures of $[\text{Co}(\text{trans-1,2-}i\text{chxn})_3]^{3+}$ used in this study: Δ -($\lambda\lambda\lambda$), Δ -($\lambda\lambda\delta$), Δ -($\lambda\delta\delta$) and Δ -($\delta\delta\delta$). These structures are shown in Fig. 1, with views along the screw axis of the three-bladed propeller formed by the chelate rings. Note that the Δ -($\lambda\lambda\lambda$) and Δ -($\delta\delta\delta$) structures each have trigonal dihedral (D_3) point-group symmetry, with a trigonal axis coincident with the propeller screw axis. The Δ -($\lambda\lambda\delta$) and Δ -($\lambda\delta\delta$) structures each have C_2 point-group symmetry, with a two-fold symmetry axis that is perpendicular to the propeller screw axis.

The structural features of $\text{Eu}(\text{dpa})_3^{3-}$ and $\text{Tb}(\text{dpa})_3^{3-}$ complexes are described in some detail elsewhere [2,8,11]. Suffice it to say here that the *dpa* ligands are achiral, and they form planar bicyclic chelate rings with the lanthanide ion. The complexes have D_3 symmetry, and their three bicyclic chelate rings form a three-bladed propeller with either a left-handed (Λ) or right-handed (Δ) screw sense. In neutral aqueous

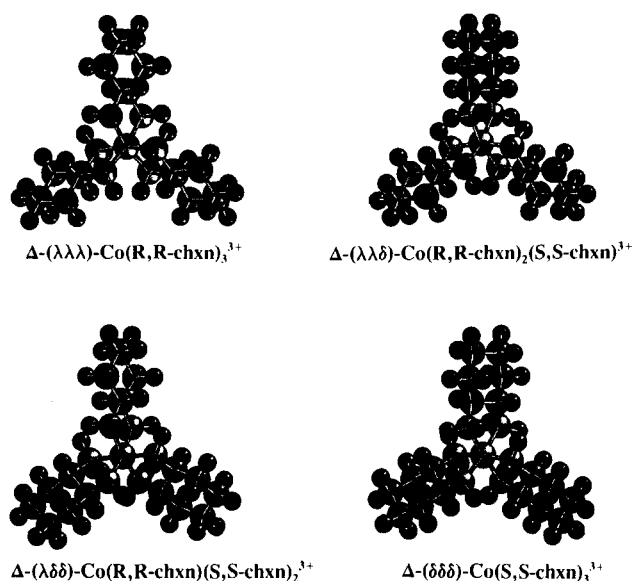


Fig. 1. Structural representations of the four cobalt(III) complexes used in this study. Views down the three-fold propeller axis are shown.

solution, the complexes exist as a racemic mixture of interconverting Λ and Δ enantiomers. Enantiomer interconversion occurs via an intramolecular, ligand-rearrangement mechanism, and at room temperature, the unimolecular rate constant for $\Lambda \rightleftharpoons \Delta$ interconversion processes is *ca.* 20 s^{-1} [11]. This rate constant is more than an order of magnitude smaller than the emission decay constants for $\text{Eu}(\text{dpa})_3^{3-}$ (5D_0) and $\text{Tb}(\text{dpa})_3^{3-}$ (5D_4) complexes in aqueous solutions (at room temperature), and we may assume, therefore, that $\Lambda\text{-Ln}(\text{dpa})_3^{3-} \rightleftharpoons \Delta\text{-Ln}(\text{dpa})_3^{3-}$ processes are much slower than the excited-state quenching processes examined in the present study.

2. Experimental section

2.1. Sample preparation

Stock solutions of $\text{Eu}(\text{dpa})_3^{3-}$ and $\text{Tb}(\text{dpa})_3^{3-}$ complexes were prepared according to procedures described previously [8]. Diastereomeric structures of $[\text{Co}(\text{trans-1,2-}i\text{chxn})_3]^{3+}$ were synthesized and resolved following methods reported by Harnung *et al.* [12]. All diastereomers were characterized by UV-visible absorption, circular dichroism, and ${}^1\text{H}$ and ${}^{13}\text{C}$ NMR measurements. The samples used in our excited-state (luminescence) quenching experiments contained a 10 mM concentration of either $\text{Eu}(\text{dpa})_3^{3-}$ or $\text{Tb}(\text{dpa})_3^{3-}$ in neutral aqueous solution with a 10 μM concentration of quencher species.

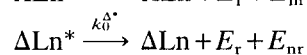
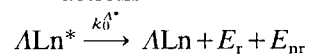
2.2. Enantiodifferential excited-state quenching measurements

These measurements were carried out using time-resolved chiroptical luminescence (TR-CL) techniques that have been described previously [2,7,8]. All measurements were performed on solution samples held at a constant temperature of 20 °C. Sample excitation was at either 465.8 nm (for $\text{Eu}(\text{dpa})_3^{3-}$ luminophores) or 488.0 nm (for $\text{Tb}(\text{dpa})_3^{3-}$ luminophores), and TR-CL measurements were made at emission wavelengths of 594.8 nm (for Eu) and 543.7 nm (for Tb).

3. Results and discussion

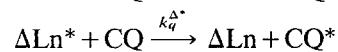
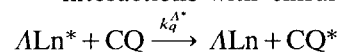
Analyses of the data obtained from our TR-CL measurements yield rate constants for the following processes:

(a) radiative and non-radiative decay of the ΔLn^* and ΔLn^* luminophores in the absence of quencher actions



where E_{r} and E_{nr} denote radiative and non-radiative energies, respectively.

(b) de-excitation of ΔLn^* and ΔLn^* via bimolecular interactions with chiral quencher (CQ) species



The two processes shown in (a) must have identical rate constants, and we can write $k_0^{\Delta^*} = k_0^{\Delta^*} \equiv k_0$. However, the two processes shown in (b) will, in general, have different rate constants ($k_{\text{q}}^{\Delta^*} \neq k_{\text{q}}^{\Delta^*}$) reflecting differences between ΔLn^* -CQ and ΔLn^* -CQ interactions (*i.e.* chiral discriminatory luminophore-quencher interactions).

In Table 1, we list the values obtained in this study for k_0 and the enantiospecific bimolecular quenching constants, $k_{\text{q}}^{\Delta^*}$ and $k_{\text{q}}^{\Delta^*}$. Also listed are values for the mean quenching constant, defined by $k_{\text{q}} = 1/2(k_{\text{q}}^{\Delta^*} + k_{\text{q}}^{\Delta^*})$, and the enantioselectivity quenching parameter, defined by $E_{\text{q}} = (k_{\text{q}}^{\Delta^*} - k_{\text{q}}^{\Delta^*}) / (k_{\text{q}}^{\Delta^*} + k_{\text{q}}^{\Delta^*})$. The magnitude and sign of the latter parameter (E_{q}) indicate, respectively, the degree and sense of enantioselectivity in the quenching processes. The degree and sense of this enantioselectivity are also reflected in the $k_{\text{q}}^{\Delta^*} / k_{\text{q}}^{\Delta^*}$ ratios shown in Table 1.

The quenching results given in Table 1 exhibit a number of rather remarkable (and surprising) features. First we note that the Eu^* and Tb^* data sets are very similar with respect to both the quencher-dependent trends and quantitative values of the various quenching parameters. This is somewhat surprising given the large

differences between $\text{Eu}^{3+}(4f^6)$ and $\text{Tb}^{3+}(4f^8)$ energy-level structures, and between Eu^* versus Tb^* emission spectra (in regions that overlap Co^{III} absorption spectra) [8]. The mean quenching constants for Tb^* are uniformly larger than those for Eu^* , but the differences are less than 15%. The magnitudes of the enantioselectivity parameter (E_{q}) are larger for Eu^* compared to Tb^* quenching, but the differences are again small. Overall, the results presented in Table 1 indicate very little differentiation between Eu^* and Tb^* quenching by the Co^{III} complexes examined in this study. However, these results show remarkable differentiation with respect to the dependence of quenching efficiency and enantioselectivity on the stereochemical details of the Co^{III} complexes.

All of the Co^{III} complexes used as quenchers in this study have the same net charge (3+), and they have essentially identical molecular sizes and electronic state structures. Moreover, they all have Δ configurational chirality, with their chelate rings forming a three-bladed propeller of right-handed screw sense. Given this commonality of primary structural properties among the complexes, one might anticipate finding little or no differentiation among them as quenchers. The results shown in Table 1 demonstrate, dramatically, that this is not the case. Variations are observed in both the degree and sense of quenching enantioselectivity (E_{q}), and in the values of the mean quenching constant (k_{q}), determined for the different quenchers. These variations can only be explained in terms of quenching processes that are extraordinarily sensitive to stereochemical structure dictated by ligand asymmetry and chelate-ring conformational chirality. We note, especially, that the values of E_{q} are strongly correlated with the relative numbers of λ versus δ chelate-ring conformations in the quencher structures.

The Δ -($\lambda\lambda\lambda$) cobalt complex exhibits a strong preference for ΔLn^* (over ΔLn^*) quenching, whereas the Δ -($\lambda\lambda\delta$), Δ -($\lambda\delta\delta$) and Δ -($\delta\delta\delta$) complexes all show a preference for ΔLn^* (over ΔLn^*) quenching. The degree of enantioselectivity exhibited by Δ -($\delta\delta\delta$) in its quenching of ΔEu^* and ΔEu^* complexes is truly remarkable. It corresponds to a 7.2:1 preference for ΔEu^* versus ΔEu^* quenching, and indicates extraordinarily strong chiral discriminatory interactions between $\text{Eu}(\text{dpa})_3^{3-}$ and Δ -($\delta\delta\delta$)-[$\text{Co}(\text{S,S-chxn})_3$] $^{3+}$ complexes.

Space limitations preclude further discussion of our results in terms of possible mechanisms and structural determinants of intermolecular chiral discrimination processes. Instead, we close by emphasizing the value of $\text{Eu}(\text{dpa})_3^{3-}$ and $\text{Tb}(\text{dpa})_3^{3-}$ complexes as luminescent probes of chirality-dependent intermolecular interactions in solution. The results obtained in this study demonstrate that enantiomers of these complexes can

TABLE 1. Rate parameters determined from TR-CL measurements of enantiodifferential excited-state quenching kinetics in solution^a

Luminophore	Quencher ^b	k_0 (s ⁻¹)	$k_q^{A^*} \times 10^{-7}$ (M ⁻¹ s ⁻¹)	$k_q^{\Delta^*} \times 10^{-7}$ (M ⁻¹ s ⁻¹)	$k_q \times 10^{-7}$ (M ⁻¹ s ⁻¹)	$k_q^{\Delta^*}/k_q^{A^*}$	E_q^c
$\text{Eu}(\text{dpa})_3^{3-}$ (⁵ D ₀)	Δ -($\lambda\lambda\lambda$)	620	11.4	3.2	7.3	0.28	-0.56
	Δ -($\lambda\lambda\delta$)	620	4.4	5.5	5.0	1.25	0.11
	Δ -($\lambda\delta\delta$)	620	2.2	9.6	5.9	4.36	0.63
	Δ -($\delta\delta\delta$)	620	0.44	3.2	1.8	7.27	0.77
$\text{Tb}(\text{dpa})_3^{3-}$ (⁵ D ₄)	Δ -($\lambda\lambda\lambda$)	474	12.6	4.1	8.4	0.33	-0.51
	Δ -($\lambda\lambda\delta$)	474	5.2	6.3	5.8	1.21	0.09
	Δ -($\lambda\delta\delta$)	474	2.8	9.8	6.3	3.50	0.56
	Δ -($\delta\delta\delta$)	474	0.56	3.2	1.9	5.71	0.70

^aAll measurements were carried out on neutral aqueous solution samples (at 20 °C) in which the $\text{Ln}(\text{dpa})_3^{3-}$ concentration was 10 mM and the quencher concentration was 10 μM. ^bDiastereomers of $[\text{Co}(\text{trans-1,2-chxn})_3]^{3+}$, labelled according to their configurational chirality (Δ) and their mixture of chelate ring conformational chiralities (λ and/or δ). See Fig. 1 for structural representations of these diastereomers. ^cEnantioselectivity quenching parameter defined by $E_q = (k_q^{\Delta^*} - k_q^{A^*}) / (k_q^{\Delta^*} + k_q^{A^*})$.

“read” and distinguish between very subtle structural features of dissymmetric quencher molecules.

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References

- 1 D.H. Metcalf, S.W. Snyder, S. Wu, G.L. Hilmes, J.P. Riehl, J.N. Demas and F.S. Richardson, *J. Am. Chem. Soc.*, **111** (1989) 3082.
- 2 D.H. Metcalf, S.W. Snyder, J.N. Demas and F.S. Richardson, *J. Am. Chem. Soc.*, **112** (1990) 5681.
- 3 R.B. Rexwinkel, S.C.J. Meskers, J.P. Riehl and H.P.J.M. Dekkers, *J. Phys. Chem.*, **96** (1992) 1112.
- 4 R.B. Rexwinkel, S.C.J. Meskers, H.P.J.M. Dekkers and J.P. Riehl, *J. Phys. Chem.*, **96** (1992) 5725.
- 5 R.B. Rexwinkel, S.C.J. Meskers, J.P. Riehl and H.P.J.M. Dekkers, *J. Phys. Chem.*, **97** (1993) 3875.
- 6 F.S. Richardson, D.H. Metcalf and D.P. Glover, *J. Phys. Chem.*, **95** (1991) 6249.
- 7 D.H. Metcalf, J.M. McD. Stewart, S.W. Snyder, C.M. Grisham and F.S. Richardson, *Inorg. Chem.*, **31** (1992) 2445.
- 8 D.H. Metcalf, J.P. Bolender, M.S. Driver and F.S. Richardson, *J. Phys. Chem.*, **97** (1993) 553.
- 9 F.S. Richardson, *Chem. Rev.*, **79** (1979) 17.
- 10 Y. Saito, *Inorganic Molecular Dissymmetry*, Springer-Verlag, Berlin, 1979.
- 11 D.H. Metcalf, S.W. Snyder, J.N. Demas and F.S. Richardson, *J. Am. Chem. Soc.*, **112** (1990) 469.
- 12 S.E. Harnung, B.S. Sorensen, I. Creaser, H. Maegaard, U. Pfenninger and C.E. Schaffer, *Inorg. Chem.*, **15** (1976) 2123.