Generation of Optical Activity by Photoinduced Chiroselective Electron Transfer

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Summary Quenching of the phosphorescence of Δ-Ru(bipy)$_3^{2+}$ (bipy = 2,2′-bipyridyl) by racemic Co(acac)$_3$ (Hacac = acetylacetone) leads to concomitant decay of the isotropic absorbance of Co(acac)$_3$ and to appearance of the c.d. absorption of Δ-Co(acac)$_3$.

DESPITE extensive research on Ru(bipy)$_3^{2+}$ (bipy = 2,2′-bipyridyl) and its derivatives,[1] problems relating to optical activity have, with only a few exceptions,[2] been ignored. It is known that Ru(bipy)$_3^{2+}$ is relatively stable thermally and photochemically in aqueous solution,[3] and it has been assumed also to be stable to racemization.[2]

We have established, in fact, that this complex does photoracemize with a small but measurable quantum yield.[4] In the course of some experiments to explore the mechanism of this racemization, we used Co(acac)$_3$ (Hacac = acetylacetone) as a quencher. Co(acac)$_3$ quenches the luminescence of Ru(bipy)$_3^{2+}$ with a rate constant of $6{\cdot}6 \times 10^8$ $\text{l mol}^{-1}\,\text{s}^{-1}$ (ref. 5) ($1{\cdot}1 \times 10^9$ l mol^{-1} in ref. 6) at room temperature in aqueous solution, and the quenching is accompanied by formation of Co^{2+} and oxidation products of acetylacetonate ion.[6]

We irradiated Δ-Ru(bipy)$_3^{2+}$ at 458 nm in the presence of Co(acac)$_3$ ($3{\cdot}3 \times 10^{-3}$ M), and observed quenching of luminescence and of racemization of Ru(bipy)$_3^{2+}$, and also generation of the c.d. spectrum of Co(acac)$_3$. The Figure shows the growth of this spectrum with increasing irradiation. At the same time the isotropic spectrum of Co(acac)$_3$ decays. Because the photoracemization of Ru(bipy)$_3^{2+}$ is only partly quenched (the concentration of quencher is limited by its low solubility in water), and because Co(acac)$_3$ itself is disappearing, the c.d. spectrum of the latter goes through a maximum and subsequently decreases to zero.

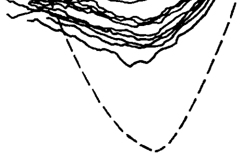

FIGURE. (a) C.d. spectrum of Co(acac)$_3$ (I. Jonas and B. Norden, *Inorg. Nuclear Chem. Letters*, 1976, **12**, 43). (b) Evolution of c.d. spectrum of Co(acac)$_3$, photosensitized by Δ-Ru(bipy)$_3^{2+}$.

These data demonstrate that the electron transfer from the triplet charge transfer state of Ru(bipy)$_3^{2+}$ to Co(acac)$_3$ takes place with a chiral selectivity, in which the Δ form of Ru(bipy)$_3^{2+}$ interacts preferentially with Λ-Co(acac)$_3$. The initial rate of growth of the Δ-Co(acac)$_3$ c.d. spectrum amounts, on a molecular basis, to 4% of the rate of decay of the isotropic spectrum. Thus the electron transfer rates to the Λ and Δ forms are in the ratio of 13 to 12. Evidence for such an effect as reported by Sutter and Hunt[7] was subsequently refuted by Kane-Maguire[8] *et al.* Work by Irie *et al.*[9] indicates even greater chiroselectivity in some energy transfer processes, but they did not generate optical activity.

The rate constant for the quenching reaction (for racemic donor and acceptor) is about one order of magnitude less than diffusion controlled. We expect that the chiroselectivity we have observed here would not occur for quenchers that are diffusion controlled.

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