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Intramolecular Energy Transfer in Osmium (II) Complexes†

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Although energy migration in rare-earth chelates has been the subject of many investigations in recent years,[1] the phenomenon of intramolecular energy transfer in transition-metal compounds has received little attention. Recently a study of the luminescence of ruthenium(II) complexes has been reported in which d–d luminescence from the Ru(II) ion was observed whenever excitation of the complexes was carried out in the $\pi \rightarrow \pi^*$ absorption bands characteristic of the ligands.[2] Thus, energy transfer from the ligand π system to the 4d-electronic system of the central chelated ion was demonstrated. The present communication reports the first observation of intramolecular energy transfer in analogous Os(II) compounds, where the transfer is from the ligand π-electronic system to the 5d-electronic states of the Os(II) ion.

Tris complexes of osmium(II) with 2,2′-bipyridine and 1,10-phenanthroline and the bis(2,2′,2″-terpyridyl)osmium(II) complex were prepared as the iodides and subjected to extensive purification for spectroscopic studies. Absorption spectra of the compounds were obtained at 25° C in water and at 77° K in methanol–ethanol (1:4 by volume). All compounds exhibited similar absorption spectra consisting of strong (molar extinction coefficient, $\epsilon \sim 10^5$) ligand $\pi \rightarrow \pi^*$ bands from 3200 to 2000 Å, a prominent ($\epsilon \sim 10^4$) charge-transfer (CT) transition peaking at ~4500 Å, and two less

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intense peaks ($\epsilon \sim 4000$) at ~ 5600 and ~ 6500 Å (Fig. 1). These latter transitions appear in all three compounds with comparable energies and intensities and are assigned to d–d transitions of the Os(II) ions.

Luminescence measurements were made by dissolving a complex in the methanol–ethanol solvent, freezing the solution to a clear glass at 77°K, and irradiating in the strong absorption bands described above. Regardless of the nature of the excitation ($\pi \rightarrow \pi^*$ or $d \rightarrow \pi^*$), the emission observed was always the same. It consisted of an intense electronic transition in the near infrared which has a prominent ($\Delta\nu = 1300$ cm^{-1}) vibrational progression and a short life, $\tau < 10^{-5}$ sec (Fig. 1). The position of the emission and its insensitivity to changes of ligand strongly support assigning it to a d–d transition which is the inverse of the lowest-energy absorption band observed for the compounds.

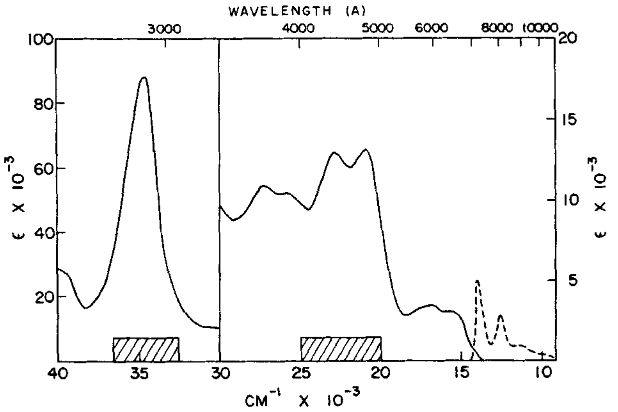

Figure 1. Absorption and emission spectra of tris(2,2′-bipyridyl)osmium(II) iodide. (——) Absorption spectrum in water at 25° C; (– – – –) emission spectrum from methanol–ethanol glass at 77° K (in arbitrary units); (▨) transmittance (in arbitrary units) of filter systems used to excite luminescence.

The experimental energy-level schemes for all three compounds are displayed in Fig. 2. The similarities among the three are striking. It is evident that pumping of energy into the ligand electronic systems is followed by transfer to the 5d-electronic levels of the Os(II) ion from which emission occurs.

Although the emission appears to be d–d in nature, the exact symmetry identification of the upper state is not clear. On an octahedral scheme and ignoring spin-orbit coupling, one would expect the $(5d)^6$ configuration of the Os(II) ion to yield a $^1A_1$ ground state and $^3T_1$, $^3T_2$, $^1T_1$, $^1T_2$ excited states in analogy with the $(4d)^6$ case for Ru(II). The emission would thus be expected to arise from either the $^3T_1$ or $^1T_1$ state, since these are the expected lowest levels of their respective multiplicities in the complexes. On the basis of previous work on Ru(II), $^1T_1$ is the suspected assignment; however, the strong spin-orbit coupling inherent in an atom of such high atomic number raises considerable doubt about the appropriateness of an LS coupling description for any transition.

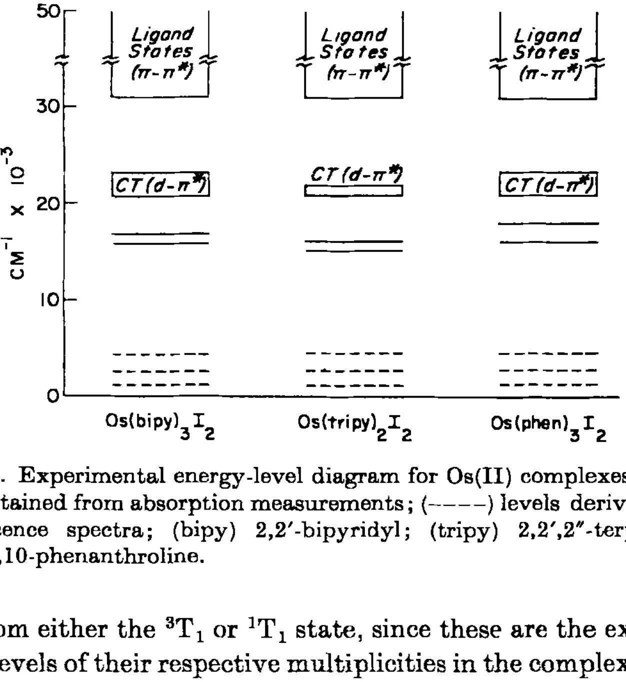

Figure 2. Experimental energy-level diagram for Os(II) complexes. (——) levels obtained from absorption measurements; (- - - -) levels derived from luminescence spectra; (bipy) 2,2′-bipyridyl; (tripy) 2,2′,2″-terpyridyl; (phen) 1,10-phenanthroline.

We are investigating other complexes of Os(II) spectroscopically, especially complexes where the symmetry is primarily tetragonal, and where radiationless transitions between singlet and triplet states are expected to be enhanced. Lifetime measurements are also in progress, and studies of the relevance of ligand-field models and LS coupling schemes for describing these molecules are underway.

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