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Luminescence Spectra of Some Ruthenium(II) Complexes

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Luminescence spectra and luminescence lifetimes have been obtained for several ruthenium(II) complexes in rigid glasses at 77 K. Complexes which have been studied are $[Ru(dipy)(py)_4]^{2+}$, *cis*- and *trans*-$[Ru(dipy)_2(py)_2]^{2+}$, *cis*- and *trans*-$[Ru(dipy)(py)_2(phen)]^{2+}$, $[Ru(dipy)(phen)_2]^{2+}$, $[Ru(dipy)(py)_2en]^{2+}$, $[Ru(dipy)(py)_2(PMA)]^{2+}$, $[Ru(dipy)(PMA)_2]^{2+}$, $[Ru(dipy)(py)_2(PEA)]^{2+}$, $[Ru(dipy)(py)_2(NH_3)_2]^{2+}$ and $[Ru(dipy)(py)_3Cl]^{+}$ (dipy = 2,2′-dipyridyl, py = pyridine, phen = 1,10-phenanthroline, en = ethylenediamine, PMA = 2-aminomethylpyridine, and PEA = 2-aminoethylpyridine).

With two exceptions the emission spectra are all very similar with band maxima near 17 000 and 16 000 cm^{-1}. $[Ru(dipy)(PMA)_2]^{2+}$ and $[Ru(dipy)(py)_2(NH_3)_2]^{2+}$ exhibited "anomalous" spectra showing different intensity ratios. The spectra are all classified as ligand $\pi^* \rightarrow$ metal *d* charge transfer type. Lifetimes are all near 10 μs; several of the decay curves showed a deviation from first order behaviour indicating a weak coupling between the ligands.

Since 1959 when Paris and Brandt reported the first observation of luminescence from a ruthenium(II) complex [1] there have been a number of papers published dealing with this topic. Most of these reports, with only a few exceptions, involved ruthenium(II) complexes containing 2,2′-dipyridyl (or the essentially identical ligand, 1,10-phenanthroline). Unfortunately, the luminescence research which has been reported to date covers a range of complexes with very little ligand, or structural, variety and few conclusions may be drawn regarding qualitative relationships. To obtain luminescence data on a broader range of complexes we have initiated the present research.

Since several ruthenium(II) complexes containing two or three dipyridyls are known to emit it was felt wise to start at this point. We have varied the coligands making several complexes based on the parent compound [1] $[Ru(dipy)(py)_4]^{2+}$. Phosphorescence spectra and luminescence lifetimes at 77 K are reported here.

EXPERIMENTAL

Complexes were prepared as already described.[2]

Luminescence measurements were made on samples dissolved in an ethyleneglycol; water glass (2:1) (approx. 10^{-3} M) in quartz tubes immersed in liquid nitrogen. Excitation was with the 3371 Å line of an Avco nitrogen laser firing at 100 pulses per second. A filter in the laser beam (Jena UG-11) removed higher orders. Emission from the sample was focused through appropriate lenses onto the entrance slit (slit width approximately 100 μ) of a Jarrell Ash 0.5 meter monochromator. The light from the monochromator went directly into an EM1-95580A photomultiplier (S-20 response). PMT output went to a Keithley 414S picoammeter and then to an appropriate recorder. Spectra are uncorrected.

Lifetimes were determined by sending the signal from the PMT into a Tektronix type 454 oscilloscope which functioned as a 10:1 preamplifier; this output went into a PAR Boxcar Integrator (Model 160) using a 0.5 μs aperture time and an appropriate time base (generally 20 or 50 μs). Triggering of the boxcar was by means of a presignal from the laser signal generator; the cable for the trigger signal also went to the oscilloscope for triggering, where it was terminated in a 50 ω load resistor. Output from the boxcar went through a voltage divider into a recorder.

In order to avoid saturation of the PMT and consequent distortion of the luminescence decay curves it was found to be necessary to adjust the monochromator slit width so that

Table 1. Emission maxima and lifetimes at 77 K.

Compound	ν_1 (in 1000 cm)	ν_2	ν_3	τ_1 (in μs)	τ_2 [a]
$[Ru(dipy)(py)_4](ClO_4)_2$	17.1	16.0		10.9 [b]	9.8 [b]
cis-$[Ru(dipy)_2(py)_2](ClO_4)_2$	17.2	16.0		11.4 [b]	10.3 [b]
trans-$[Ru(dipy)_2(py)_2](ClO_4)_2$	17.1	15.9		10.6 [b]	10.4 [b]
cis-$[Ru(dipy)(py)_2(phen)](ClO_4)_2$	17.3	16.2		14.8	13.2 [b]
trans-$[Ru(dipy)(py)_2(phen)](ClO_4)_2$	17.0	15.9		8.0 [b]	8 [b]
$[Ru(dipy)(phen)_2](ClO_4)_2$	17.4	16.1	16.5	15.8	15.1
$[Ru(dipy)(py)_2en](ClO_4)_2$	17.2	15.8		10.9 [b]	9.8 [b]
$[Ru(dipy)(py)_2PMA](ClO_4)_2$	17.2	16.1	16.4	10.6 [b]	10.2 [b]
$[Ru(dipy)(PMA)_2](ClO_4)_2$	16.3	15.4	17.4	9.0 [c]	7.8 [c]
$[Ru(dipy)(py)_2(PEA)](ClO_4)_2$	17.2	16.0		11.3 [b]	9.6 [b]
$[Ru(dipy)(py)_3Cl](ClO_4)$	17.2	15.7		10.5	[c]
$[Ru(dipy)(py)_2(NH_3)_2](ClO_4)_2$	16.0	17.2	15.0	[c]	9.3

[a] ν_1 most intense; ν_3 weakly resolved, shoulder, or very weak. τ_1 is the emission lifetime at ν_1. [b] First order decay plot shows some curvature, with initial slope generally within 25 % of the least squares value. [c] First order decay plot nonlinear.

the maximum signal reaching the boxcar was less than 370 mV. These slit widths were all near 100 μ.

Least squares analysis was applied to the data to determine the lifetime value, assuming first order decay.

RESULTS AND DISCUSSION

As first suggested by Paris and Brandt [1] all of the emission spectra are most likely of the charge transfer type, ligand $\pi^* \rightarrow t_2$ metal orbital. Thus the emission spectrum reflects the properties of the low lying excited charge transfer states and the vibrational spectrum associated with the ground electronic state.

The lifetimes of the excited states are approximately 10 μs. An interesting feature emerges in that the first order decay plots of a number of the emission peaks deviate from linearity, most only slightly but several to a great extent (Table 1). This could be caused by several factors, one of which is the possibility of a manifold of decaying excited states in thermal equilibrium. Harrigan and Crosby [3] have suggested such a condition from a study of $Ru(dipy)_3^{2+}$ and two related complexes. Recently, Hager and Crosby [4] studied computer fit temperature dependence data and presented a model involving at least three closely lying emitting excited states. Lifetimes of 10 μs are rather short for spin-singlet→spin-triplet transitions and quite long for singlet→singlet transitions. In accord with the proposal of Crosby, Hipps and Elfring [5] we take it that the spin-orbit coupling has done away with S as a good quantum number for the excited states.

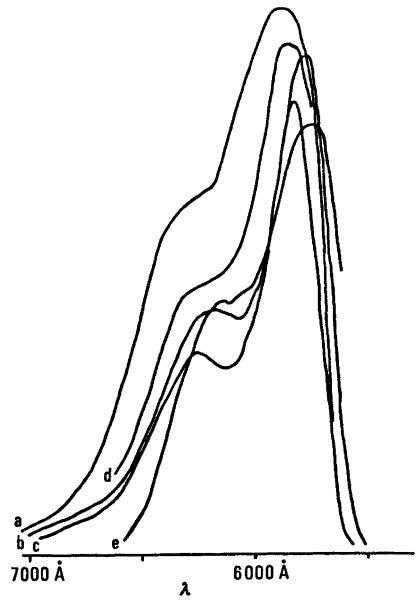

Fig. 1. Emission spectra in ethylene glycol-water glass at 77 K. (Intensities offset for clarity). a, *trans*-$[Ru(dipy)(py)_2(phen)](ClO_4)_2$; b, *cis*-$[Ru(dipy)(py)_2(phen)](ClO_4)_2$; c, *cis*-$[Ru(dipy)_2(py)_2](ClO_4)_2$; d, *trans*-$[Ru(dipy)_2(py)_2](ClO_4)_2$; e, $[Ru(dipy)(phen)_2](ClO_4)_2$.

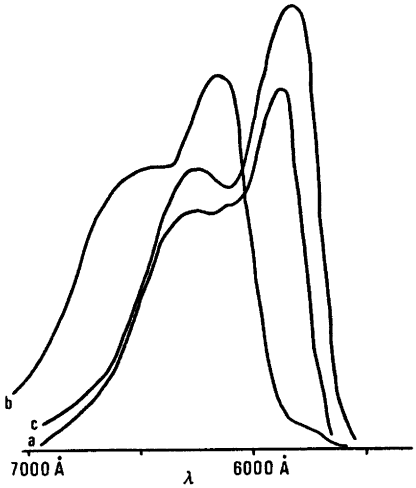

Fig. 2. Emission spectra in ethylene glycol-water glass at 77 K. (Intersities offset for clarity). a, $[Ru(dipy)(py)_2PMA](ClO_4)_2$; b, $[Ru(dipy)(PMA)_2](ClO_4)_2$; c, $[Ru(dipy)(py)_2PEA](ClO_4)_2$.

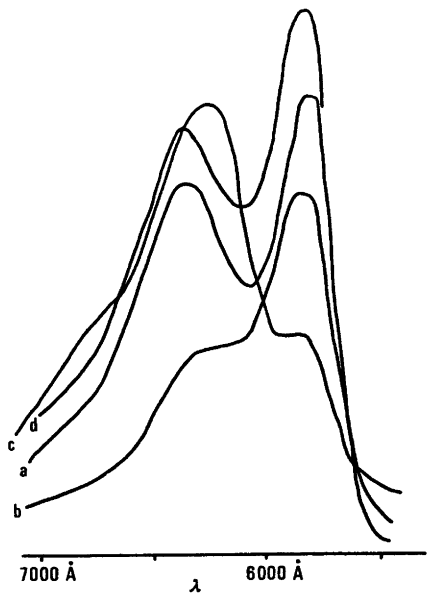

Fig. 3. Emission spectra in ethylene glycol-water glass at 77 K. (Intensities offset for clarity). a, $[Ru(dipy)(py)_2en](ClO_4)_2$; b, $[Ru(dipy)(py)_4](ClO_4)_2$; c, $[Ru(dipy)(py)_2(NH_3)_2](ClO_4)_2$; d, $[Ru(dipy)(py)_3Cl](ClO_4)$.

With two exceptions the emission spectra reflecting the ground state vibrations of the complexes under study are all very much alike. They are characterized by a band near 17 000 cm^{-1} and a second, weaker band at 16 000 cm^{-1}. In two cases a third component is visible between the two major peaks. The two *cis-trans* pairs are very much alike in band position, band shape, and relative intensities. Replacing one aromatic amine group with the aliphatic NH_2 of PMA or PEA leaves the basic emission spectrum relatively unchanged. Replacing two aromatic amine groups with one ethylenediamine is also without effect.

Two of the spectra are anomalous in that they depart from the form of those of the other ten compounds. $[Ru(dipy)(PMA)_2](ClO_4)_2$ has an emission which is red shifted by about 1000 cm^{-1} from the other complexes. $[Ru(dipy)(py)_2(NH_3)_2](ClO_4)_2$ has a different shape to its emission spectrum, the highest energy band being of lower intensity than the principle peak at 16 000 cm^{-1}.

Most of the ruthenium(II) complexes which have been observed to emit contain dipyridyl or phenanthroline. The few exceptions are the complex with tripyridyl [6,7] a complex with di(quinolyl)pyridine[8] (although both of these really would be expected to be identical with dipyridyl), ruthenocene [9] and possibly [10] $[Ru(\phi_2PCH_2CH_2P\phi_2)_2]Cl_2$ (later workers could not detect emission from this compound [11]). Klassen *et al.*[8] did however observe a case of apparent steric influence in that the lifetime of the di(quinolyl)pyridine complex was significantly reduced below that of the tripyridyl compound (4.7 *vs.* 10.7 μs).

With an electronic excitation into one of the π ligand systems a competition between three processes occurs. The molecule can revert to its ground state *via* a radiationless transition, it can emit from the lowest excited state of the ligand in question or the excitation can spread out over the entire π network of all three ligands before the system goes back to the ground state. It is clear that when the electronic coupling is weak, and the excitation remains localized the emission spectrum will be rather unaffected by the unexcited ligands. If on the other hand the electronic coupling is strong and a delocalization is the dominat-

ing process an entirely new situation is met with.

Both of these extremes have been reported previously. Halper and DeArmond [12] in a study of some rhodium(III) complexes observed a nonlinear decay and concluded multiple emissions, from localized triplets, to be the cause. Recently Crosby and Elfring [13] concurred with this; however, in the same study these latter authors concluded there to be strong ligand-ligand electronic coupling in a set of ruthenium(II) complexes.

The accumulated evidence in the present study points toward a weak coupling. With the excited state being primarily a spin-triplet the energy transfer from one ligand to another is a slow process, and the excitation remains localized for many periods of ligand vibrations. The majority of emission spectra from mixed complexes should in this case be observed as superpositions of bands from their "parent" species. The existence of a weak coupling from one ligand to another produces a second channel for relaxation which again will lead to a non-linear decay law. Hence the majority of the investigated complexes are seen to fall in the weak coupling limit. For the complexes which fall outside this general pattern more detailed spectra than can be obtained at liquid nitrogen temperatures would be needed in order to settle the nature of the electronic couplings between the ligands.

One final comment on our results is pertinent; that is the dependence of emission properties on molecular geometry. While the *cis* and *trans* isomers of $[Ru(dipy)_2(py)_2]^{2+}$ are nearly identical in emission lifetimes and presumably have the same electronic symmetry, the *cis* and *trans* isomers of $[Ru(dipy)(py)_2(phen)]^{2+}$ show considerably different lifetimes. At this point it is difficult to conclude the exact meaning of this, but further studies, of a wide variety of compounds, is certainly called for.

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