Quantum Efficiencies on Transition Metal Complexes. II. Charge-Transfer Luminescence[1a]

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Abstract: Absolute luminescence quantum yields and lifetimes in a rigid alcoholic glass at 77°K have been measured for six ruthenium(II), three osmium(II), and one iridium(III) complex containing either 2,2′-bipyridine, 1,10-phenanthroline, or 2,2′,2′′-tripyridine as ligands. Some yields ranged as high as 0.5–0.6. An intrinsic lifetime, τ_0, a radiative rate constant, k_r, and a quenching rate constant, k_q, have been determined for each complex. Evidence for a near-unity efficiency for population of the emitting level following optical pumping of any upper excited state was obtained. A semiempirical spin–orbit-coupling model gave semiquantitative predictions of trends in τ_0's for related complexes and adds support to the assignment of these charge-transfer emissions to principally a spin-forbidden process, at least at 77°K. Radiative lifetimes for emitting states have been evaluated by use of the Einstein and Strickler–Berg formulas. The values were one to two orders of magnitude smaller than the same quantities derived from the quantum-yield measurements.

Compounds exhibiting d–d luminescences appear to be well characterized experimentally, and the orbital and spin descriptions of the emitting levels seem to be readily rationalized. In contrast, the assignment of the orbital and spin labels to the emitting levels of substances producing charge-transfer (CT) luminescence has been a much more difficult problem.

Indeed, even confirmation of the assignment of the emission from tris(2,2′-bipyridine)ruthenium(II) as a charge-transfer luminescence has been a most elusive goal. Originally, this emission was tentatively assigned as a charge-transfer fluorescence;[2] subsequently, Porter and Schläfer described the process as a ligand-field (d–d) phosphorescence.[3] Later, Crosby, Perkins, and Klassen[4] proposed a d–d fluorescence assignment based on the appearance of a very weak absorption transition (assigned to a $^1A_{1g} \rightarrow {}^3T_{1g}$ transition in octahedral microsymmetry) at longer wavelengths than the emission; this weak band was shown to arise from an impurity, and the question was reopened.

The assignment of the luminescence from ruthenium(II) complexes to a charge-transfer process was finally confirmed by Klassen and Crosby by means of a comprehensive study on a series of ruthenium(II) molecules.[5] A d–d assignment was eliminated by demonstrating that a crystal-field model was not capable of explaining the observed trends in emission energies. In addition the emission energies were shown to follow the strong visible absorption bands which were obviously charge transfer in character. No decision was made, however, concerning the multiplicity of the emitting states. Zuloaga and Kasha[6] also assigned the luminescences of several Ru(II) [and Os(II)] molecules to charge-transfer transitions, basing their argument on the similarities between the structures of the emissions and the charge-transfer absorption bands and on the dissimilarities between the observed emission bands and the d–d emissions observed from other d^6 complexes. They postulated that the emissions were fluorescences, *i.e.*, singlet–singlet transitions.

The CT luminescence of ruthenium complexes was assigned to a spin-forbidden process by this laboratory.[7] The assignment of a triplet-spin label to the emitting states rested on the magnitudes of the observed lifetimes (0.5–10 μsec) and the presence of a unique luminescence band from a given complex. The usually short lifetimes of the luminescences from the complexes were attributed to a strong heavy-atom perturbation of the emitting triplet state rather than to a low quantum yield. Lytle and Hercules[8] subsequently confirmed that the absolute yield of $[Ru(bipy)_3]^{2+}$ at 77°K was high; they also assigned the luminescence to a phosphorescence, *i.e.*, a triplet–singlet transition.

Currently, the experimental evidence strongly supports the contention that the CT emissions from ruthenium(II) complexes are principally spin forbidden in character, at least at 77°K. Similar, although less extensive, evidence exists for assigning the CT emissions from analogous osmium(II) and iridium(III) complexes to spin-forbidden processes.

In the present article we assume the luminescences observed from these complexes to be charge transfer in character and, at low temperature, mainly spin-forbidden processes. The current study adds corroborative evidence for these assignments, supplies quantitative information on the rates and efficiencies of the relaxation processes in these types of d^6 molecular systems, and supplements the information already available for d^6 complexes displaying d–d luminescences.[9]

Experimental Section

Table I lists all the complexes investigated. The $[Ru(bipy)_3]Cl_2$ from G. Frederick Smith Chemical Co. was used without further purification. The $Ru(CN)_2(bipy)_2$ was a sample prepared by

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[2] J. P. Paris and W. W. Brandt, *J. Amer. Chem. Soc.*, **81**, 5001 (1959).

[3] G. B. Porter and H. L. Schläfer, *Ber. Bunsenges. Phys. Chem.*, **68**, 316 (1964).

[4] G. A. Crosby, W. G. Perkins, and D. M. Klassen, *J. Chem. Phys.*, 43, 1498 (1965).

[5] D. M. Klassen and G. A. Crosby, *ibid.*, **48**, 1853 (1968).

[6] F. Zuloaga and M. Kasha, *Photochem. Photobiol.*, **7**, 549 (1968).

[7] J. N. Demas and G. A. Crosby, *J. Mol. Spectrosc.*, **26**, 72 (1968).

[8] F. E. Lytle and D. M. Hercules, *J. Amer. Chem. Soc.*, **91**, 253 (1969).

[9] J. N. Demas and G. A. Crosby, *ibid.*, **92**, 7262 (1970).

Table I. Quantum Yields, Lifetimes, and Rate Constants for Ruthenium(II), Osmium(II), and Iridium(III) Complexes in an Alcohol Glass[a] at 77 °K

Complex[b]	Quantum yield[c] Q	Lifetime τ, μsec	Intrinsic lifetime[d] τ_0, μsec	Radiative rate constant[d] $k_r \times 10^{-4}$, sec^{-1}	Quenching rate constant[e] $k_q \times 10^{-4}$, sec^{-1}
$[Ru(bipy)_3]Cl_2$	0.376 ± 0.036	5.21[f]	13.9	7.19	12.0
$[Ru(phen)_3]I_2$	0.584 ± 0.065	9.79[f]	16.8	5.95	4.26
$[Ru(tripy)_2]I_2$	0.479 ± 0.027	10.66[f]	22.3	4.48	4.90
cis-$[Ru(CN)_2(bipy)_2]$	0.269 ± 0.008	3.96[f]	14.7	6.80	18.4
$[Ru(en)(bipy)_2]I_2$	0.0222 ± 0.0009	0.96	43.2	2.32	102
$[Ru(ox)(bipy)_2]$	0.0124 ± 0.0009	0.61	49.2	2.03	162
$[Os(bipy)_3]I_2$	0.0348 ± 0.0020	0.89	25.6	3.91	109
$[Os(phen)_3]I_2$	0.126 ± 0.009	2.43	19.3	5.18	36.0
$[Os(tripy)_2]I_2$	0.124 ± 0.0015	3.88 ± 0.07	31.3	3.20	22.6
cis-$[IrCl_2(phen)_2]Cl$	0.496 ± 0.017	6.92 ± 0.05	14.0	7.14	7.31

[a] Ethanol–methanol glass (4:1, v/v). [b] Abbreviations of ligands: bipy = 2,2′-bipyridine; phen = 1,10-phenanthroline; tripy = 2,2′,2′′-tripyridine; en = ethylenediamine; ox = oxalate. For proper chemical names and formulas see Experimental Section and references therein. [c] Absolute accuracy is estimated to be ±30%. [d] Calculated from eq 1. [e] Calculated from eq 2. [f] Average of values reported in ref 7.

Demas, Turner, and Crosby,[10] and the iridium complex was prepared by Carstens.[11] The remaining ruthenium complexes were taken from samples prepared and studied by Klassen and Crosby.[5] The solvents and their purification procedures were the same as reported previously.[9] All solutions were saturated with air, since earlier work[7] suggested that oxygen quenching did not occur significantly in low-temperature glasses. At room temperature oxygen quenched some of the complexes; however, since only wavelength dependences of the quantum yields were measured, this was of no consequence.

The instrumentation and calibration procedures used for this study have been described earlier.[9] For the wavelength-dependence studies on $[Ru(bipy)_3]Cl_2$ and for those measurements on $[Os(tripy)_2]I_2$ which go beyond 600 nm, however, a Hitachi MPF-2A spectrofluorimeter was used. Calibration of the excitation monochromator source was accomplished with an Eppley 12-junction linear bismuth–silver thermopile. Blanks were run in all measurements.

The relative yield of $[Ru(bipy)_3]Cl_2$ at room temperature was measured by an optically dense method (optical density greater than 10/cm). A 1-cm cuvette filled with a concentrated solution of the complex was placed at the focus of the excitation monochromator, while the luminescence was viewed from its backside by an EMI 9558QC phototube, mounted off axis. The blocking filters over the phototube were a Corning 2-59 and 1.5 cm of aqueous $[Fe(bipy)_3]Cl_2$ (0.6 g/l.). Relative quantum yields were computed by eq 1a of part I[9] (using the approximation $10^{-A(\lambda)L} = 0$). The remaining relative quantum-yield measurements were made by the optically dilute method ($A \leq 0.01$), and the yields were calculated using eq 1b of part I.[9] The excitation band pass was 5.0 nm for measurements made on the Hitachi and 5.5 nm for those made on the infrared-sensitive instrument.

All emission spectra and absolute quantum yields were obtained using 436-nm excitation (5.5-nm band pass for yields). For the yield determinations stray light above 450 nm was reduced by an Optics Technology 450 blue-edge blocking filter, while extraneous radiation below 420 was largely eliminated by a Corning 3-73 filter (ruthenium complexes) or by Corning 3-73 and 3-74 filters (osmium species). For emission and yield measurements concentrations ($0.2\text{–}5 \times 10^{-5}$ *M*) were low enough to avoid the necessity for reabsorption corrections. Absolute yields were determined by an optically dilute relative method using a fluorescein standard. Part I[9] discusses the relevant experimental details, the numerous corrections, and the formula employed (eq 3 of ref 9); the accuracy of these procedures is estimated to be only ±30%, mainly because of possible cumulative systematic errors.

Except for $[Ru(en)(bipy)_2]I_2$ and $[Ru(ox)(bipy)_2]$ the lifetimes of ruthenium complexes were taken from our published data;[7] the values of Table I are averages of the several values previously reported. The instrumentation used for measuring the lifetimes of the remaining complexes is discussed elsewhere.[7] In all but the iridium case, the standard excitation filter system was 1.5 cm of aqueous $CuSO_4 \cdot 5H_2O$ (100 g/l.) plus a Corning 7-60 glass filter (320–400-nm excitation). Our sample of iridium complex was, however, slightly impure as shown by its nonexponential decay when excited in this spectral region. Since 436-nm excitation was used in the quantum-yield measurement on this complex, it was deemed necessary to have the lifetime under similar conditions. To effect this the excitation filter was changed to a 10-nm band pass Balzers 437-nm narrow-band interference filter followed by a Corning 7-59 glass filter. Under 436-nm excitation the decay was exponential, which indicated that the impurity was not excited efficiently at this wavelength. All lifetimes shorter than 4 μsec were calculated by numerical curve fitting or by the methods of moments.[12] The reliability of these short lifetimes is estimated to be ±15% for all except the oxalato complex, where a probable error of ±20% is more realistic.

Results

Table I lists the quantum yields and lifetimes for all the substances. Also included are radiative (k_r) and quenching (k_q) rate constants and the computed intrinsic lifetimes (τ_0). These quantities were calculated by means of the equations

$$k_r = 1/\tau_0 = Q/\phi_{isc}'\tau \qquad (1)$$

$$k_q = (1/\tau)[1 - (Q/\phi_{isc}')] \qquad (2)$$

which are analogous to eq 4 and 5 of part I, but the meaning of ϕ_{isc}' must be somewhat modified (see below). For these calculations the yield for population of the emitting state from the pumping state (ϕ_{isc}') was assumed to be unity for all the molecules.

The relative quantum yield and absorption spectrum of $[Ru(bipy)_3]Cl_2$ at room temperature and at 77 °K are given in Figures 1 and 2. Corresponding data are shown for $[Os(phen)_3]I_2$ in Figure 3 and for $[Os(tripy)_2]I_2$ in Figure 4. Only in the case of the $[Os(tripy)_2]I_2$ at room temperature was excitation carried to wavelengths longer than 600 nm. Figure 5 displays the low-temperature absorption spectrum and the relative yield of $[Os(bipy)_3]I_2$. These last data are less reliable than those for the other molecules.

Discussion

The Nature of the Low-Lying Excited States. The complexes of Ru(II) and Os(II) have visible absorption spectra and emission spectra which possess the same gross features. Both series display intense

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(10) J. N. Demas, T. F. Turner, and G. A. Crosby, *Inorg. Chem.*, **8**, 674 (1969).

(11) D. H. W. Carstens, Ph.D. Dissertation, University of New Mexico, Albuquerque, N. M., 1969.

(12) J. N. Demas and G. A. Crosby, *Anal. Chem.*, **42**, 1010 (1970).

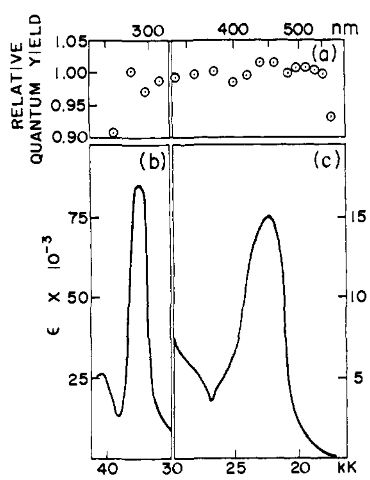

Figure 1. Relative quantum yield (a) and absorption spectrum (b, c) of tris(2,2′-bipyridine)ruthenium(II) chloride in methanol at room temperature: (a) 0.2 g/5 ml in a 1-cm cell, (b, c) 6.7 × 10^{-5} *M* in a 1-cm cell. The first and last yield points are less accurate than the others.

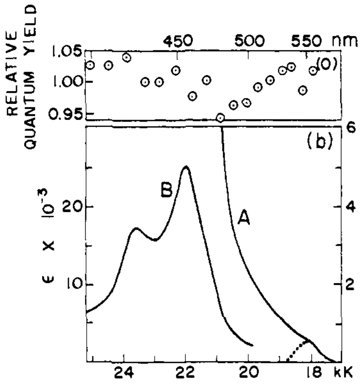

Figure 2. Relative quantum yield (a) and absorption spectrum (b) of tris(2,2′-bipyridine)ruthenium(II) chloride in an ethanol–methanol glass (4:1, v/v) at 77°K: (a) 3.4 × 10^{-7} *M* in a 1.76-cm cell; (b) curve A (right-hand scale), 1.32 × 10^{-4} *M* in a 1.76-cm cell; curve B (left-hand scale), 2.65 × 10^{-5} *M* in a 1.76-cm cell. Dotted curve is the estimated contribution of the singlet–triplet absorption.

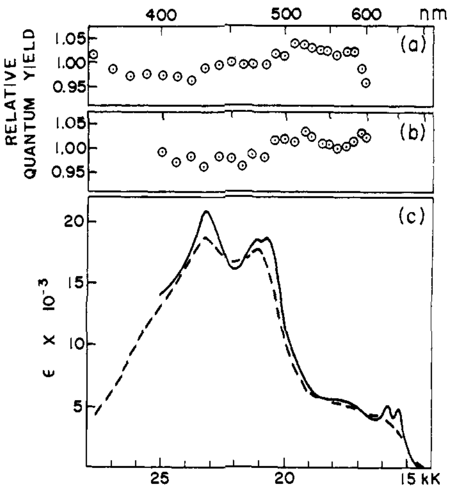

Figure 3. Relative quantum yields (a, b) and absorption spectra (c) of tris(1,10-phenanthroline)osmium(II) iodide in ethanol–methanol (4:1, v/v): (a) 4.5 × 10^{-7} *M* in a 1.76-cm cell at room temperature; (b) 4.5 × 10^{-7} *M* in a 1.76-cm cell at 77°K (glass); (c) ---, 9.0 × 10^{-6} *M* in a 10-cm cell at room temperature; ——, 7.12 × 10^{-6} *M* and 1.42 × 10^{-5} *M* in 1.76-cm cells at 77°K (glass).

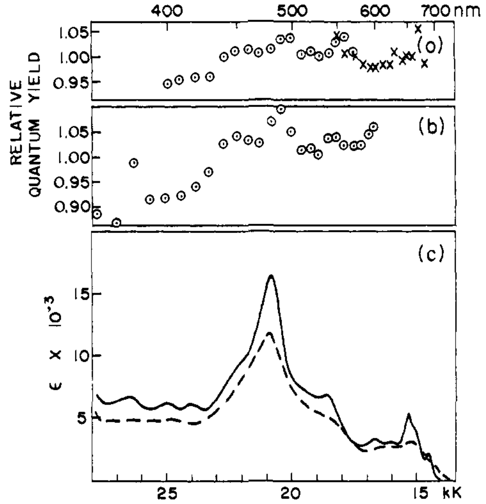

Figure 4. Relative quantum yields (a, b) and absorption spectra (c) of bis(2,2′,2″-tripyridine)osmium(II) iodide in ethanol–methanol (4:1, v/v): (a) ⊙, 6.9 × 10^{-7} *M* in a 1.76-cm cell at room temperature; ×, 2.3 × 10^{-6} *M* in a 1-cm cell (Hitachi MPF-2A; solvent, methanol only) at room temperature; (b) 6.9 × 10^{-7} *M* in a 1.76-cm cell at 77°K (glass); (c) ---, 1.37 × 10^{-5} *M* in a 10-cm cell at room temperature; ——, 6.55 × 10^{-5} *M* and 1.31 × 10^{-5} *M* in 1.76-cm cells at 77°K (glass).

charge-transfer absorption bands at energies lower than the ligand $\pi-\pi^*$ transitions, and each compound displays a unique strong luminescence at 77 °K which has a prominent vibrational progression and a short lifetime (~0.5–10 μsec). The first strong absorption band (ϵ ~10,000–20,000) is generally broad and virtually structureless at room temperature, and its maximum is removed by a considerable energy from the onset of the emission band. For ruthenium complexes the luminescence overlaps the tail of the absorption spectrum little or not at all.[5] In contrast, all the osmium molecules are distinguished by the presence of a series of absorption peaks of moderate intensity (ϵ ~4000) which span the region between the first intense absorption peak and the luminescence. Overlap of absorption and luminescence is prominent.[13] The visible absorption spectrum of the iridium complex differs considerably from those of the other two series. The bands assigned as charge transfer occur only as shoulders on the first prominent $\pi-\pi^*$ transition with intensities less than 2000. The emission spectrum definitely overlaps the tail of the absorption and displays the prominent well-defined vibrational progression (1.4 kK interval) characteristic of CT luminescences from molecules with these ligands.[5,11]

Although all these ions have d^6 electronic configurations, charge-transfer absorption bands, and apparently charge-transfer emission spectra, the relative importance of oxidation state, oxidation potential, and spin–orbit coupling in determining the nature and sequence of the excited states in the various molecules certainly varies drastically, and it is risky to push analogies among them too far. We will attempt to build a model to account satisfactorily for the presently available evidence, to exploit the analogies which appear reasonable, and to delineate clearly where we believe these generalizations may fail.

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(13) B. J. Pankuch and G. A. Crosby, unpublished data.

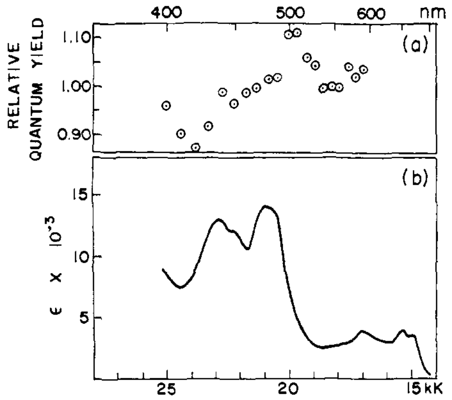

Figure 5. Relative quantum yield (a) and absorption spectrum (b) of tris(2,2′-bipyridine)osmium(II) iodide in an ethanol–methanol glass (4:1, v/v) at 77°K: (a) 7.2×10^{-7} M in a 1.76-cm cell, (b) 6.73×10^{-5} M and 1.35×10^{-5} M in 1.76-cm cells.

The experimental evidence derived from luminescence measurements indicates that the lowest excited state is formally a d–π^* triplet state in the Ru(II) and Ir(III) molecules. Spin–orbit coupling splits the triplet into two or three components. The splitting is small for ruthenium molecules (10–20 cm^{-1}) and somewhat larger for iridium species.[14] The lowest lying excited state for the Os(II) molecules is probably $^3(\text{d}-\pi^*)$ also, but the obvious new features in the low-energy region of the Os(II) absorption spectra and the radical changes in the Os(II) luminescence properties at very low temperatures (<30°K)[15] indicate that the detailed disposition of Os(II) low-lying excited states may prove to be fundamentally different from those of Ru(II) and Ir(III).

The intense main absorption band which is present in the ruthenium and osmium molecules signals the occurrence of a highly allowed electronic transition. We interpret this absorbance as the onset of the first spin-allowed CT transition which is strongly orbitally allowed, *i.e.*, $^1\text{A}_1 \rightarrow {}^1(\text{d}-\pi^*)$. *Other singlet transitions lower in energy but only weakly allowed* may be present but are overlapped too strongly to be clearly identified. At much higher energies π–π^* transitions can be seen. For the iridium(III) complex the first really intense absorption lies in the uv and is mainly π–π^*, but it is overlapped by CT transitions of moderate intensity. Because of the lack of knowledge concerning energies, intensities, and spin designations of states which lie between the emitting level(s) and the first highly allowed level where optical pumping occurs, it is not possible for us to distinguish experimentally between intersystem crossing (relaxation between states of different multiplicities) and internal conversion (relaxation between states of the same multiplicity). Indeed, especially for iridium and osmium, where spin–orbit coupling is large, such labeling may be deceiving. For these reasons we use the term ϕ_{isc}' in eq 1 and 2 to designate the efficiency of relaxation from the singlet excited state reached by light absorption and the manifold of thermally populated emitting states (vibrational, spin orbit, or electronic).

Relaxation Efficiencies. Essential to a quantitative determination of the radiative and quenching rate constants for depopulation of the emitting level is a value for ϕ_{isc}'. For all of our computations we assumed a value of unity for this quantity, an assumption based on the following experimental information.

In Figure 1 the results of a room-temperature relative-quantum-yield measurement on a solution of $[\text{Ru(bipy)}_3]\text{Cl}_2$ are shown. To at least 17.7 kK (the approximate maximum of the lowest energy absorption band discernible at 77°K) there is no increase in the relative yield. Thus, at room temperature there is no evidence for a ϕ_{isc}' less than unity. This result is not impeccable, however. Since the weak absorption band is not resolved, it is impossible to tell what fraction of the absorbed light excites molecules directly to the triplet manifold. Consequently, the invariance of the yield could be attributed to virtually total absorption by the tail of the strongly allowed transition or to excitation of a weak singlet nearby. In view of the very low extinction coefficient in the red region (ϵ <400), this objection does not seem too serious. A second criticism of our interpretation of the invariance of the quantum yield in this region stems from the fact that a near coincidence of singlet and triplet levels could possibly occur and promote S–T thermal crossover at 300°K.[16] Thus, even if ϕ_{isc}' were unity at room temperature, it might be much smaller at 77°K. To test this latter hypothesis, the 77°K optically dilute measurement of the molecule (Figure 2) was carried out. If the dotted-in curve represents the approximate position and intensity of the absorption band inverse to the emission, as seems reasonable both from the shape of the absorption curve and from the strong overlap of the emission with this band, then there is no evidence for a low ϕ_{isc}' at 77°K. From a consideration of the constancy of the quantum yield with wavelength, the experimental spread in the measurements, and the probable fraction of the exciting light being absorbed in the band inverse to the emission, ϕ_{isc}' is estimated to be greater than 90%, and it is believed to be unity at 77°K. This complex is typical of the ruthenium compounds, and consequently it is reasonable to assume that $\phi_{\text{isc}}' \sim 1.0$ for all the other ruthenium complexes at liquid nitrogen temperature. It is important to note that if $\phi_{\text{isc}}' \sim 1.0$ and the emission is predominantly a phosphorescence, the intersystem-crossing yield must also be on the order of unity.

The results of similar experiments on the osmium complexes are shown in Figures 3–5. There is no evidence for a low ϕ_{isc}' in any of the Os(II) complexes at 77°K or at room temperature. Furthermore, for the one case where a measurement was carried out to 680 nm (Figure 4a), the yield does not increase at the longer wavelengths. If the relatively weak structured absorption bands in the 500–700-nm region can be assigned to an unusually well-resolved, heavy-atom-perturbed $\text{S}_0 \rightarrow \text{T}$ absorption and there are no singlet states falling in the lower energy range investigated, then ϕ_{isc}', the intersystem-crossing yield, must be on the order of unity. Thus it seems probable that under our conditions ϕ_{isc}' and possibly even ϕ_{isc} in osmium complexes are also within 10–15% of unity.

To determine the efficiency of relaxation between π–π^* states and an emitting d–π^* charge-transfer state

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(14) R. J. Watts, R. W. Harrigan, and G. A. Crosby, *Chem. Phys. Lett.*, **8**, 49 (1971).

(15) R. W. Harrigan and G. A. Crosby, unpublished data.

(16) E. C. Lim, J. D. Laposa, and J. M. H. Yu, *J. Mol. Spectrosc.*, **19**, 412 (1966).

only one experiment was carried out. The molecule chosen was $[Ru(bipy)_3]Cl_2$. Figure 1 shows the result. There is no evidence for an increase or decrease in the quantum yield when excitation occurs in the $\pi-\pi^*$ singlet band *vs.* excitation in the prominent $d-\pi^*$ singlet band.

These data rule out the possibility of significant quenching to the ground state from the levels through which the molecule passes as it loses energy. Since relaxation from the lowest allowed $^1(d-\pi^*)$ to the $^3(d-\pi^*)$ emitting manifold of excited states is believed to proceed with unit efficiency, then we conclude that $(\pi-\pi^*) \rightarrow (d-\pi^*)$ relaxation has nearly unit efficiency also. From our measurements one cannot distinguish between the probable paths $^1(\pi-\pi^*) \rightsquigarrow {}^1(d-\pi^*) \rightsquigarrow {}^3(d-\pi^*)$ and $^1(\pi-\pi^*) \rightsquigarrow {}^3(\pi-\pi^*) \rightsquigarrow {}^3(d-\pi^*)$.

That relaxation between $\pi-\pi^*$ and $d-\pi^*$ states would be rapid is not surprising in view of the fact that a $d-\pi^*$ state function contains a large admixture of π character. Since the two types of wave functions have a considerable degree of common π parentage, it seems likely that relaxation between these states would be efficient (relaxation between $\pi-\pi^*$ levels of aromatic molecules in condensed media almost always proceeds with unit efficiency). Similarly, it would be reasonable to assume that relaxation between $d-\pi^*$ and lower d–d levels would also be rapid since both wave functions contain a large component of d character. The efficiency of direct relaxation from $\pi-\pi^*$ to d–d levels, either by internal conversion or intersystem crossing, has not yet been measured. Since the wave functions are spatially separated and have different parentage, such relaxation might be appreciably hindered (see part I). More experimental evidence is required to settle this question.

Rate Constants. It is of interest to determine the actual magnitude of k_{isc}', the rate of relaxation from the highly allowed $^1(d-\pi^*)$ state to the $^3(d-\pi^*)$ emitting manifold. Although it is not possible to determine k_{isc}' directly in these compounds, since they do not fluoresce from the $^1(d-\pi^*)$ levels reached by direct excitation, it is possible to set lower limits on k_{isc}' by making suitable approximations.

An intense ($\sim$15,000) $^1A_1 \rightarrow {}^1(d-\pi^*)$ transition lies at $\sim$470 nm in the osmium complexes. Because of the strongly allowed nature of this transition k_f, the radiative rate of depopulation of this $^1(d-\pi^*)$ state, would probably be very rapid; 10^7 sec^{-1} is a reasonable lower limit since almost all orbitally allowed fluorescences have rate constants higher than this value. From our measurements the fluorescence quantum yield from this state is at least 10^3 times smaller than the observed phosphorescence yield in the 2,2′,2″-tripyridine and 1,10-phenanthroline complexes. Since the phosphorescence yield is about 0.1 for these compounds, the fluorescence quantum yield (ϕ_f) from the allowed $^1(d-\pi^*)$ level must be less than 10^{-4}. ϕ_f is related to fundamental rate constants by

$$\phi_f = k_f/(k_f + k_{isc}' + k_q) \qquad (3)$$

where k_q is the rate for nonradiative quenching of this state directly to the ground state and k_{isc}' is the sum of the rate constants for intersystem crossing to the triplet manifold and for internal conversion to lower excited singlet states. Since the crossing yield is estimated to be near unity, k_{isc}' is much greater than k_q. Therefore, based on the values for ϕ_f and k_f estimated above, k_{isc}' must be greater than 10^{11} sec^{-1}. Even if k_f were really only 10^6 sec^{-1}, the lower limit for k_{isc}' would still be 10^{10} sec^{-1}. A lower limit of 5×10^{10} sec^{-1} for intersystem crossing has been set by Lytle and Hercules for $[Ru(bipy)_3]Cl_2$ using similar arguments. Comparable values are expected for the other CT emitters.

We wish to emphasize that the k_{isc}' estimated above could actually represent *either* an intersystem-crossing constant *or* an internal-conversion constant, even if S were a good quantum number. If the strongly allowed $^1(d-\pi^*)$ state is really the lowest excited singlet state in the complex, then k_{isc}' does represent an intersystem-crossing rate. If, however, this $^1(d-\pi^*)$ level is not the lowest singlet state, then k_{isc}' can be interpreted as an intersystem-crossing rate, an internal-conversion rate, or a combination of the two, depending upon the relaxation mechanism assumed. We have as yet no unambiguous information about intersystem-crossing rates in these molecules.

A Spin–Orbit-Coupling Model. Since the quantum-yield measurements permit an evaluation of radiative decay constants for the emitting states of the molecules, it is of interest to develop a model to rationalize the observed trends in τ_0 values and to make predictions of τ_0 values for analogous molecules containing these elements. Since the determination of spectroscopic parameters from first principles is not a realistic goal, we have adopted a semiempirical approach in which only the spectroscopic properties of the molecules and the atomic properties of the component elements are utilized in the calculation.

For an emitting triplet state a formula relating the intrinsic life to the absorption intensity is[17]

$$1/\tau_0 = K'E_T{}^2\int \epsilon_T d\bar{\nu} \qquad (4)$$

where τ_0 = the intrinsic lifetime of the emitting state, K' = a constant, E_T = the energy of the emitting state above the ground state, ϵ_T = the molar extinction coefficient of the transition connecting the ground state with the emitting state, and $\bar{\nu}$ = the energy in kilokaisers. The integration is carried out over the entire absorption band inverse to the emission.

Since the singlet–triplet absorption band which we assume to be the inverse of the luminescence is not clearly resolvable in these molecules, we have chosen to calculate the $S_0 \rightarrow T$ absorption intensity from a measurement of the intensity of the spin-allowed band from which the intensity is assumed to be "borrowed," the energy gap between the two excited states, and an empirical spin–orbit-coupling matrix element connecting the emitting and the "perturbing" state.

From perturbation theory[18] we have

$$\int \epsilon_T d\bar{\nu} = (E_T/E_S)[|M_{SO}|^2/(E_T - E_S)^2]\int \epsilon_S d\bar{\nu} \qquad (5)$$

where ϵ_S = the molar extinction coefficient of the singlet–singlet transition from which the triplet "borrows" its intensity, E_S = the energy of the perturbing singlet state, and M_{SO} = the spin–orbit-coupling

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[17] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 174.

[18] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962, p 191.

matrix element connecting the perturbing singlet and the emitting triplet state.

This formula is based on the assumption that only one singlet state contributes significantly to the intensity observed for the singlet–triplet transition. If two or more states with different energies and intensities are really involved, the computations as described here are invalid, or at best one must think of the quantities as average values. Substitution of eq 5 into eq 4 yields the relation

$$1/\tau_0 = K'(E_T{}^3/E_S)[\,|M_{SO}|^2/(E_T - E_S)^2]\int \epsilon_S d\bar{\nu} \quad (6)$$

One must choose the mixing singlet. Because of the squared energy term in the denominator, significant mixing between states of widely different energies is not expected. Because of the small energy separation involved, the most reasonable choice for the mixing singlet was presumed to be the state responsible for the first prominent charge-transfer absorption band. The energy of the first absorption maximum of this highly allowed band ($\epsilon > 10^4$) was taken as E_S.

The next problem concerns the evaluation of the integral, since the observed band might be made up of several overlapping transitions. To simplify we set

$$\int \epsilon_S d\bar{\nu} = K''\epsilon(E_S) \quad (7)$$

where K'' = a constant and $\epsilon(E_S)$ = the molar extinction coefficient at energy E_S. Although the bandwidths of the prominent CT transitions are not the same for all the molecules considered, K'' is assumed to have the same value for all the osmium and ruthenium complexes. Any errors introduced by this assumption are overshadowed by the approximate nature of the equations.

Only evaluation of E_T remains. Since the singlet–triplet absorption band is not resolved at all in some cases, emission data were used to estimate this term. E_T was assumed to be the energy of the shortest wavelength emission peak. This procedure is consistent and is probably reasonably accurate. From these data the term $K|M_{SO}|^2$ ($K = K'K''$) was calculated for each molecule. Table II shows the pertinent quantities and the results.

Table II. Spin–Orbit-Coupling Matrix Elements in Osmium and Ruthenium Complexes at 77°K

Complex	E_S, kK	E_T, kK	ϵ	$E_S - E_T$, kK	$K\|M_{SO}\|^2 \times 10^7$ [a]
$[Ru(bipy)_3]Cl_2$	22.02	17.12	20,100	4.90	3.78
$[Ru(phen)_3]I_2$	22.22[b]	17.62	21,000[b]	4.60	2.43
$[Ru(tripy)_2]I_2$	21.05[b]	16.62	12,900[b]	4.43	3.13
cis-$[Ru(CN)_2(bipy)_2]$	21.19[b]	17.12	9,810[b]	4.07	4.85
$[Ru(en)(bipy)_2]I_2$	19.76[b]	14.78	14,400[b]	4.98	2.44
$[Ru(ox)(bipy)_2]$	19.23[b]	14.19	11,100[b]	5.04	3.13
$[Os(bipy)_3]I_2$	20.92	14.09	14,900	6.83	9.16
$[Os(phen)_3]I_2$	20.83	14.48	18,500	6.35	7.74
$[Os(tripy)_2]I_2$	20.92	14.28	16,300	6.64	6.20

[a] $K|M_{SO}|^2$, (mol cm)/(l. μsec), computed from eq 6. Intrinsic lifetimes taken from Table I. [b] Values from D. M. Klassen, Ph.D. Dissertation, University of New Mexico, Albuquerque, N. M., 1966.

A perusal of Table II shows that $K|M_{SO}|^2$ is remarkably constant for all the ruthenium complexes and also for all the osmium complexes. The results also indicate that coupling between the emitting triplet and the perturbing singlet in both the series is more a function of the central-metal ion than of the detailed structures of the ligands or of the molecular geometry. These factors will probably make this kind of semiempirical treatment of considerable predictive value in studies of other types of complexes.

One of the most gratifying results shown in Table II is that $K|M_{SO}|^2$, and presumably $|M_{SO}|^2$ also, is greater for the osmium complexes than for their ruthenium analogs—as it should be; the average increase is 2.5. The long lifetimes of the osmium complexes and, incidentally, of the oxalato and ethylenediamine complexes of ruthenium are thus traceable to the large energy separations between their interacting states which reduce the effectiveness of the perturbing singlets even though the spin–orbit coupling is larger in the molecules containing the heavier element.

The increase in the $K|M_{SO}|^2$ on going from ruthenium to osmium is not, however, as large as would be predicted from theory. Subject to several stringent assumptions, $K|M_{SO}|^2$ should be proportional to ξ^2, where ξ is the spin–orbit-coupling constant for the metal d electrons.[19] When extrapolated values[20] for ruthenium(II) and osmium(II) of 1.1 and 3.0 kK, respectively, are used, an increase of 7.5 would be expected compared with the observed 2.5.

Several reasons could be invoked for explaining the apparent reduction of spin–orbit coupling in osmium molecules with respect to ruthenium species. First, osmium complexes could have a higher degree of covalency than the analogous ruthenium ones. Covalency would reduce the spin–orbit coupling constant because of the greater delocalization of the d electrons onto the ligands. The less the electron feels the heavy-metal nucleus, the smaller ξ is. Secondly, the assumption that the radiative rate constant is proportional to the integral of ϵ_T over the entire mixing singlet band could lead to discrepancies. This assumption would be valid only if all the components of the triplet state were equally involved in the emission process, since the intensity of the absorption band calculated by eq 5 would be the intensity of the triplet band summed over all its components. In osmium the spin–orbit interactions are probably large enough to separate the components of the triplet so that not all levels are thermally populated at 77°K. If this occurred one or more of the possible radiative paths for depopulation of the triplet state would be cut off, and the intrinsic lifetime derived from eq 2 would be longer than that evaluated from the absorption measurements. We note also that τ_0 would not be uniquely defined. If several states are in thermal equilibrium, τ_0 represents a weighted (Boltzmann) average of their individual decay constants; consequently τ_0 may vary with temperature. Finally, the calculation could be entirely erroneous, and the agreement only fortuitous. This last possibility seems unlikely in view of the model's success for a substantial number of compounds.

The apparent success of a spin–orbit-coupling scheme for correlating trends in the measured τ_0 values

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(19) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1969.

(20) B. N. Figgis, "Introduction to Ligand Fields," Wiley, New York, N. Y., 1966, p 60.

strongly supports the assignment of the observed luminescences to principally spin-forbidden processes, at least at 77 °K. Until the states intermediate between the lowest triplet and the first strong CT singlet in both ruthenium and osmium complexes are better characterized as to symmetries, energies, and spin labels, however, further analysis of the implications of the model would be perilous.

Because of its success it is worthwhile to see how useful the model can be for predicting the intrinsic lifetimes of new compounds. To test its predictive powers, an average value of $K|M_{SO}|^2$ was calculated from the data for the tris(2,2′-bipyridine), the tris(1,10-phenanthroline), and the bis(2,2′,2′′-tripyridine) complexes of ruthenium. Using this average value one can calculate the τ_0's of these complexes as well as of the other ruthenium complexes from eq 6 and 7. The results are given in Table III. The worst agreement (for the dicyano complex) is only ~40%. Predictions for other osmium complexes using the average matrix element value derived from the three analogous osmium complexes are also given in the table; unfortunately no quantum-yield data for cis-substituted osmium complexes are available for testing the procedure. From the good agreement achieved for the ruthenium complexes, it is reasonable to infer comparable accuracy for predictions on related cis-substituted osmium molecules.

Table III. Calculated and Observed Intrinsic Lifetimes of Ruthenium and Osmium Complexes

Compound (77 °K)	τ_0(calcd),[a] μsec	τ_0(exptl), μsec
$[Ru(bipy)_3]Cl_2$	16.9	13.9
$[Ru(phen)_3]I_2$	13.1	16.8
$[Ru(tripy)_2]I_2$	22.4	22.3
cis-$[Ru(CN)_2(bipy)_2]$	22.9	14.7
$[Ru(en)(bipy)_2]I_2$	33.9	43.2
$[Ru(ox)(bipy)_2]$	49.5	49.2
$[Os(bipy)_3]I_2$	29.8	25.6
$[Os(phen)_3]I_2$	19.0	19.3
$[Os(tripy)_2]I_2$	24.6	31.3

[a] Calculated from eq 6. The value of $K|M_{SO}|^2$ for the ruthenium complexes was taken as 3.11×10^{-7}, and for the osmium complexes a value of 7.87×10^{-7} was used.

A possible use of eq 6 and 7 is the estimation of absolute quantum yields of new ruthenium and osmium complexes of a type similar to those studied. τ_0 could be calculated from absorption and emission data; then division of the measured lifetime by this quantity would yield an estimate of the quantum yield.

A word of warning should be given regarding estimation of radiative lives by the method described here. All the compounds studied were noncentrosymmetric (D_3 symmetry or lower). In centrosymmetric complexes the lowest charge-transfer transitions may be symmetry as well as spin forbidden. Thus, the previous calculations might be invalid for centrosymmetric molecules.

Integrated Extinction Coefficients. An alternative approach for estimating intrinsic lives has gained some acceptance in the treatment of inorganic systems. The procedure is based on the Einstein integrated extinction coefficient formula (eq 4 with K' in terms of fundamental constants) which relates the intrinsic life of an emission to the absorption intensity to the state from which the emission arises.

The application of the formula for d–d or charge-transfer emissions has been based, however, more on an act of faith than on a firm experimental verification of its validity. We have tested the Strickler–Berg modification of this formula[21] on $[Ru(bipy)_3]Cl_2$ and the osmium complexes studied here. Assuming that the degeneracy factor (g_u/g_l) is unity (see ref 9), we find the experimentally determined τ_0's for charge-transfer emissions are 8 to 40 times longer than the calculated values. The Einstein formula yields even worse agreement. In part I of this series we showed that a comparable uncertainty (factor of 50) was present for at least one calculation on a d–d phosphorescence. Recent studies[14,15] suggest that, at least in the case of charge-transfer emitters, these serious discrepancies may not be fundamental but may be a result of our present inability to assess properly the contribution of various excited states to the emission and absorption processes. Because of such manifest experimental difficulties, we are not sanguine of the usefulness of the Einstein or Strickler–Berg equations for determining radiative lifetimes, at least not until these complex inorganic systems are more fully understood.

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[21] S. J. Strickler and R. A. Berg, *J. Chem. Phys.*, 37, 814 (1962).