Relaxation of Excited States in Transition-Metal Complexes

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Excited electronic states in metal complexes relax by a combination of radiative and nonradiative processes (Figure 1, Table I), with the relative magnitude of these two processes commonly deduced from emission quantum yield (Φ) and lifetime (τ) data. These photophysical processes assume fundamental significance due to their complementary relationship to the photochemical deactivation process. Knowledge of the relative rates for the various processes can permit design of transition-metal complexes that will not decompose, as required in pigment applications, or metal complexes that will photolyze, as required for pesticide or herbicide application. The role of metal complexes as quenchers of excited states in π-electron organics can be understood in detail only when these photophysical processes are understood. The function of metal ions in energy-transport processes of metal-containing biological systems begins to be delineated from studies of metal porphyrin complexes.[1,2]

To obtain useful photophysical data, three constraining criteria must be met: (1) a substantial variety of complexes involving structural variation must be available; (2) the complexes should be inert and photochemically stable: and (3) the emission must occur in a readily accessible region of the spectrum (300–1100 nm).

All three criteria are well met only by d^3 and d^6 systems and virtually no other d electron configuration.[3,4] For the d^6 configuration, in particular for the second and third series complexes, a number of complexes of Ru^{2+}, Rh^{3+}, Os^{2+}, and Ir^{3+} do luminesce.[5-8] Moreover, the significance of d^6 emitters is enhanced by the availability of two distinct energy level schemes: (1) a localized "d–d" type emitter in which the ligands are a small perturbation upon the metal levels and (2) an emitter in which delocalized levels characteristic of the ligand or with mixed d–π character emit.

Examination of some principal results and conclusions for the organic π systems indicates methods of approach to the photophysical relaxation of transition-metal complexes. In general, relative emission efficiencies have been related to the spacing and coupling of lowest excited vibronic levels with the ground-state vibronic levels.[9,10] Specifically, Φ and τ for hydrocarbons increase upon deuteration. Further, quantum yield and emission polarization data indicate that nonradiative selection rules are operative in heterocyclic systems.[9,10]

Rationale of these data by Robinson and Frosch[11] and Gouterman[12] and elaboration by others[13-15] determined that for large molecules the rate-determining relaxation step was intramolecular rather than intermolecular. Additionally, the rate constant for nonradiative deactivation, k_n, is the product of an electronic factor (vibronic or spin–orbit) and a vibrational factor. Accurate calculations of nonradiative rate constants for these complex π systems are not yet possible, but the data provided by experiment and the partial answers of theory have permitted the development of a "feedback" mechanism that allows better delineation of fundamental criteria for the production of a type of emission with a particular efficiency. The relaxation phenomena for transition-metal complexes are not so well understood. However, some experimental generalizations are available; therefore some questions can be formulated for the luminescent d^3 and heavy-metal d^6 complexes. For example: (1) Why is emission consistently observed only for d^3 and heavy metal d^6 emitters? (2) Why are "d–d" emitters typically low-efficiency emitters? (3) Why does phosphorescence (spin forbidden) emission generally predominate? (4) Do Kasha's rules apply? (a) Does emission occur only from the lowest level of given spin multiplicity? (b) Does intersystem crossing occur only from the lowest state of a given spin multiplicity? (5) How can metal complexes having low frequency vibrations ($\gamma < 500$ cm^{-1}) be efficient deactivators? (6) Do high-frequency (light atom) vibrations participate in relaxation of excited states?

Some answers begin to appear. For example, the presence of a deuterium isotope effect for the $Cr(H_2O)_6^{3+}$ species[16] is informative (question 1). The variation of quantum yield with wavelength for the $Rh(dip)_2Cl_2^+$ and $Rh(phen)_2Cl_2^+$ complexes[17] is relevant to question 4b. The significance of ligand

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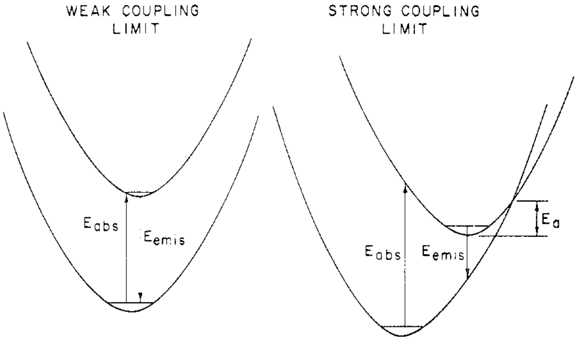

Figure 1. The vibrational coupling limits for radiationless transitions.

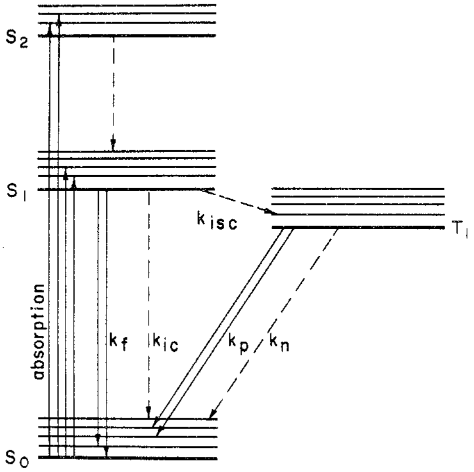

Figure 2. Level diagram showing radiative (solid lines) and nonradiative (broken lines) transitions between singlet (S) and triplet (T) states for a general metal complex.

vibrations external to the d–d chromophore (question 5) has been demonstrated by the variations in the nonradiative rate constants for the series of β-diketone chelates of Cr(III). The recognition of the significance of the weak and strong coupled classification (Figure 1) to the electronic relaxation of both d^3 and d^6 complexes[17,18] may prove useful to the structuring of the theory of relaxation of transition-metal complexes.

Therefore, the purpose of this Account will be to systematize available luminescence data for d^3 and d^6 complexes. The rationalization of the general trends will necessarily depend significantly upon the theory available for the organic π-electron systems. Indeed, a recent effort to apply, within a restrictive framework, this π-electron theory has generated some interesting conclusions.[19]

Results: the Generation of Questions

Table I
Nonradiative Transitions for d^3 and d^6 Complexes

Transition	Type of transition	Vibrational coupling
I. d^3 Complexes (O_h)		
A. Localized orbital		
$^2E \rightsquigarrow {}^4A_2$	Intersystem crossing	Weak
$^4T_2 \rightsquigarrow {}^2E$	Intersystem crossing	Strong
$^4T_2 \rightsquigarrow {}^4A_2$	Internal conversion	Strong
B. Delocalized Orbital		
II. d^6 Complexes		
A. Localized orbital (O_h)		
$^3T_1 \rightsquigarrow {}^1A_1$	Intersystem crossing	Strong or weak
$^1T_1 \rightsquigarrow {}^3T_1$	Intersystem crossing	Strong
$^1T_1 \rightsquigarrow {}^1A_1$	Internal conversion	Strong or weak
B. Delocalized orbital		
$^3S_1 \rightsquigarrow {}^1S_0$	Intersystem crossing	Weak
$^1S_1 \rightsquigarrow {}^3S_0$	Intersystem crossing	Weak
$^1S_1 \rightsquigarrow {}^1S_0{}^{\cdot}$	Internal conversion	Weak

The d^3 Configuration. Figure 2 indicates the lowest excited levels and the rate constants for the radiative and nonradiative processes for a general metal complex. Luminescence observed for d^3 complexes[20,21] is usually spin-forbidden "phosphorescence" ($^2E \rightarrow {}^4A_2$ corresponding to $T_1 \rightarrow S_0$) and is characterized by a small or zero Stokes shift, vibrational structure, and small-band half-width for low-resolution solution spectra (Table II). Fluorescence has been observed for a few complexes[22] and contrasts phosphorescency by having a broad, structureless envelope and a large Stokes shift.

The quantum yields of emission for molecular chromium complexes in glassy solvents can, with one exception, be categorized as small, in fact, approaching zero (Table III). Equations 1 and 2 derived from the steady-state assumption[20] define Φ_p and τ_p in terms of the relevant rate constants. Equations 3 and 4 derived from perturbation theory[21] permit in-

$$\tau_p = (k_p + k_n)^{-1} \tag{1}$$

$$\frac{\Phi_p}{\tau_p} = \frac{k_{isc}k_p}{k_f + k_{ic} + k_{isc}} = \Phi_{isc}k_p \tag{2}$$

$$f({}^2E \longleftarrow {}^4A_2) = \frac{4f({}^4T_2 \longleftarrow {}^4A_2)\zeta^2\overline{\nu}({}^2E \longleftarrow {}^4A_2)}{9[W({}^4T_2) - W({}^2E)]^2\overline{\nu}({}^4T_2 \longleftarrow {}^4A)} \tag{3}$$

$$k_p = \frac{2n^2f({}^2E \longleftarrow {}^4A_2)\overline{\nu^2}}{3} \tag{4}$$

dependent calculation of k_p. n = index of refraction, f = oscillator strength, and, $W(\ )$ = energy of ( ) state. From (3) and (4) the k_p constant for the $^2E \rightarrow {}^4A_2$ process can be calculated. The absence of fluorescence prevents calculation of k_{ic}. However, (2) permits insight into the relative magnitude of k_{ic}, k_{isc}, and k_f. If the calculated k_p is used in (2), then Φ_{2E} can be calculated for the complexes (Table III). Even if these values are in error by a factor of 2, the results do indicate that Φ_{2E}, the intersystem crossing yield, is less than 1, an unexpected result since **L·S** coupling is large in these complexes. The quantitative implication is that $k_f + k_{ic} \geq k_{isc}$. Moreover, the absence of measurable fluorescence further implies that $k_f \ll k_{ic}$ since $\Phi_f \sim 10^{-3}$ can be measured with most spectrometers. Forster's temperature-dependent Φ_p and τ_p data[23,24] have verified the significance of *internal conversion*, k_{ic}, in the relaxa-

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Table II
Absorption and Emission Data in Glassy Solution at Liquid N_2 Temperatures

Complex	Absorption data, 10^3 cm^{-1}		Emission data, 10^3 cm^{-1}			
	$\bar{\nu}_{max}$[d]	Assignment	$\bar{\nu}_{max}$[d]	$\bar{\nu}_{1/2}$	τ_p, μsec	Assignment
			Localized orbital			
Cr(exan)$_3$[a]	12.8	$^2E \rightarrow {}^4A_2$	12.8	0.410	380	$^2E \rightarrow {}^4A_2$
	16.4	$^4T_2 \rightarrow {}^4A_2$				
	20.4	$^4T_1 \rightarrow {}^4A_2$				
Rh(dmtc)$_3$[b]	(20.0)	$^3T_1 \rightarrow {}^1A_1$	11.6	3.0	3.5	$^3T_1 \rightarrow {}^1A_1$
	23.5	$^1T_1 \rightarrow {}^1A_1$				
	26.1	$^1T_2 \rightarrow {}^1A_1$				
[Ir(en)$_3$]Cl$_3$[c]	(34.0)	$^3T_1 \rightarrow {}^1A_1$	16.8	3.2	<10	$^3T_1 \rightarrow {}^1A_1$
	40.8	$^1T_1 \rightarrow {}^1A_1$				
	45.9	$^1T_2 \rightarrow {}^1A_1$				
			Delocalized orbital			
2,2′-Dipyridyl[c]	35.3	$^1(\pi-\pi^*) \rightarrow {}^1A_1$	(19.5)		955 × 10^3	$^3\pi^* \rightarrow {}^1\pi$
	41.0		(20.4)			
	42.5		20.7			
			21.7			
			23.1			
[Rh(dip)$_3$]Cl$_3$[c]	31.2	$^1(d-\pi^*) \rightarrow {}^1A_1$	(15.2)		221 × 10^1	$^3(d-\pi^*) \rightarrow {}^1A_1$
	32.6		(16.6)			
	41.3		(19.2)			
			19.6			
			20.7			
			22.2			

[a] Reference 18. [b] Reference 6. [c] Reference 5. [d] ( ), shoulder.

Table III
Quantum Yields and Rate Constants (sec^{-1}) for Chromium(III) Complexes in Glassy Solvents at Liquid Nitrogen Temperatures

Complex	k_p[a]	$k_n + k_{isc}$[b]	Φ_p[c]	Φ_p'[c]	Φ_p/τ	$\Phi_{^2E}$
Cr(acac)$_3$[d]	110	2300	0.019[d]	0.050	43	0.18
Cr(mxan)$_3$[e]	500	2500	0.030	0.035	80	0.17
Cr(exan)$_3$[e]	500	2300	0.044	0.048	130	0.27
Cr(dmtc)$_3$[e]	550	7600	0.018	0.013	145	0.27
Cr(dtc)$_3$[e]	550	7900	0.028	0.020	230	0.42
Cr(en)$_3^{3+}$[f]	150	9800	0.0090		90	0.60
Cr(en)$_2$Cl$_2^{+}$[f]	500	2900	0.0061		190	0.40

[a] Calculated from eq 3 and 4. ζ = 160 cm^{-1}. [b] Calculated from $(\tau_p)^{-1} = k_p + k_{isc} + k_n$. [c] Φ_p for irradiation into $^4T_2$ band. Φ_p' for irradiation into the higher energy band (Cr(exan)$_3$ 313 nm; Cr(dtc)$_3$ 313 nm; Cr(acac)$_3$ 365 nm). [d] Reference 20; acac = acetylacetone. [e] Reference 18. [f] Reference 21, en = ethylenediamine.

tion of excited states in chromium complexes. Further, the fact that some d^3 Cr^{3+} complexes show weak fluorescence[22] is verification of the significance of the spin-allowed relaxation channel to decay of d^3 excited states.

Comparison of the ratios k_{ic}/k_f and k_{isc}/k_D, for the spin-forbidden and spin-allowed process, respectively, is useful in rationalizing the relative efficiency of the two relaxation pathways. The spin-forbidden ratio is known, but only an estimate of the spin-allowed ratio is available. However, the prevalence of "phosphorescence type" emission ($0.001 \leq \Phi_p \leq 0.05$) and the estimate of $\Phi_f \leq 0.001$ suggest that $k_{ic}/k_f > k_n/k_D$; that nonradiative internal conversion is relatively more efficient than nonradiative intersystem crossing.

High-resolution spectra (4 K) are available for d^3 Cr systems in dilute single crystals and can be useful in identifying vibrational contributions to the deactivation of excited state and measuring separations of excited states. The absorption and emission ($^2E \rightarrow {}^4A_2$) spectra for an individual complex normally exhibit common vibrations with a predominance of low-energy (<500 cm^{-1}) metal-coupled modes.[25,26] The sulfur complex, Cr(exan)$_3$ (where exan = ethylxanthate), is unique in showing an extended vibrational progression in the emission, the 105-cm^{-1} progression assigned by Agarwala and Rao[27] as a C_1–O–C_2 bending mode having significant S–C_1–O character. This low-energy A_1 symmetry vibration is also prominent in the absorption transition for all three interconfiguration transitions, *i.e.*, $^2E_2 \leftarrow {}^4A_2$, $^2T_2 \leftarrow {}^4A_2$ and $^2T_1 \leftarrow {}^4A_2$. Such non-nearest-neighbor vibrational coupling to the $^2E \leftrightarrow {}^4A_2$ transition has also been observed in the oxalate complex.[26]

A diffuse band structure is observed in the spin-forbidden absorption spectra of the two sulfur chelates, Cr(exan)$_3$ and Cr(dmtc)$_3$ (where dmtc = dimethyldithiocarbamate). For the Cr(exan)$_3$ chelate, the diffuse structure at higher energies from the ^2E state can be used to located the higher energy $^2T_1 \leftarrow {}^4A_2$ transition. The $^2E \leftrightarrow {}^4A_2$ transition for Cr(dmtc)$_3$ is very diffuse, much broader than the transition for Cr(exan)$_3$ with a band half-width under low resolution twice that of the Cr(exan)$_3$ emission width (but a factor of three less than that of a pure fluorescence emission). Further, a 720-cm^{-1} Stokes shift is measured, implying that the 0–0 band is not observed. This distortion is likely indicative of strong mixing of the ^2E and $^4T_2$ states. Therefore, the emission observed here would be best described as a "fluorescence–phosphorescence." For the sequence of complexes Cr(exan)$_3$, Cr(dmtc)$_3$, and Cr(dtp)$_3$ (where dtp = diethyl dithiophosphate) the quartet–doublet band separation diminishes,[25] consistent with the observation of phosphorescence (Cr(exan)$_3$), phosphorescence–fluorescence (Cr(dmtc)$_3$), and no emission or no high-resolution $^2E \leftarrow {}^4A_2$ absorption (Cr(dtp)$_3$). Although the $^4T_2$

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Table IV
Quantum Yields and Rate Constants for d^6 Complexes[a]

Complex	Φ_p	k_p, sec^{-1}	k_n, sec^{-1}
Delocalized Orbital			
[Rh(dip)$_3$]Cl$_3$	0.29	1.3×10^2	3.1×10^2
[Rh(dip)$_2$phen]Cl$_3$	0.57 (365)[b]	1.5×10^1 [c]	1.2×10^1 [c]
	0.32 (313)[b]	1.4×10^2 [d]	2.9×10^2 [d]
cis-[Ir(dip)$_2$Cl$_2$]Cl	0.44	8.3×10^4	1.0×10^5
2,2′-Dipyridyl·HCl	0.26	2.6×10^{-1}	7.3×10^{-1}
Localized Orbital			
cis-[Rh(dip)$_2$Cl$_2$]Cl	0.018	3.8×10^2	2.1×10^4
trans-[Rh(en)$_2$Cl$_2$]Cl	0.0010	6.7×10^1	6.5×10^4
[Rh(en)$_3$]Cl$_3$	0.0093	4.4×10^2	4.8×10^4
[Ir(en)$_3$]Cl	0.002	$<2 \times 10^3$	$<1 \times 10^6$

[a] References 17, 28. [b] Excitation wavelength in nanometers. [c] Calculated using eq 1 and 2 with long (phen like) τ. [d] Calculated using eq 1 and 2 with short (dip like) τ.

$\leftarrow {}^4A_2$ absorption maximum for Cr(dtp)$_3$ is ~2000 cm^{-1} higher in energy than the ${}^2E \leftarrow {}^4A_2$ absorption, the lack of phosphorescence from this complex is explained if the ${}^4T_2$ minimum lies lower than the ${}^2E$ minimum.

The d^6 System. The d^6 series of complexes provide a range and variety of energy level schemes not possible for d^3 systems. A level scheme with the lowest excited levels deriving from d orbitals is termed *localized orbital* level while the *delocalized orbital* limiting case encompasses those complexes having either a ligand-field charge transfer or a ligand-localized level lowest in energy. This molecular orbital terminology avoids the ambiguity associated with the crystal-field terminology which designates charge-transfer transitions as $d \rightarrow \pi^*$ or $\pi \rightarrow d^*$, thus failing to recognize the mixed character of the initial and final orbitals in these systems.

Table II contains data typical for a *delocalized orbital* complex. The variation of metal from Ru(II) through Ir(III) does provide large variation in metal spin–orbit coupling and in the mixing of the d orbital. The shift of the chelate emission from that of the free ligand increases in the sequence Rh(III) < Ir(III) < Ru(II) and reflects increasing d-orbital participation in the emission orbital. For $\Psi = a\phi_{d\pi} + b\phi_{\pi}$, a for Ru(II) is larger than a_{Rh}, while a_{Ir} is perhaps intermediate in magnitude. Further, the decrease in the chelate lifetimes (Table II) from the free-ligand values reflects the contamination of the molecular orbital with d character.

The data for the mixed-ligand Rh(III) chelates Rh(dip)$_2$phen^{3+} and Rh(phen)$_2$dip^{3+} (where phen = 1,10-phenanthroline and dip = 2,2′-dipyridyl) is also assigned as *delocalized orbital* emission, but now two lifetimes are measured.[28] These data indicate that simultaneous emission is occurring from the individual chelate rings, a behavior expected when the triplet state is localized within an individual chelate ring rather than delocalizing through two or three of the chelate rings (as probably occurs for the Ru(II) case).

Quantum yields, lifetimes, and rate constants of the delocalized orbital emitters and the free ligands are tabulated in Table IV. These rate constants were calculated from eq 1 and 2 by assuming that the intersystem crossing yield, Φ_{isc} is one.[8]

The observation of nonexponential emission[29] for the glassy solutions of Rh(dip)$_3{}^{3+}$ and Rh(phen)$_3{}^{3-}$ at liquid He temperature, permitting calculation of two lifetimes, indicates that spins are polarized and therefore that there exist selection rules for intersystem crossing into and out of the emitting triplet. Comparison of 77° and 4° τ_p data and the Φ_p values for the two complexes indicates that the [Rh(dip)$_3$]$^{3+}$ complex passes a unique nonradiative process.

Since phosphorescence is a formally spin-forbidden process, a dependence of k_p upon the square of the effective spin–orbit coupling constant (ζ) (eq 5) is

$$k_p = B'[c^*_{r\mu k}c_{s\nu k}\zeta_{(\mu\nu)k}]^2 \tag{5}$$

expected, and in appropriate circumstances k_n is also dependent upon ζ^2 (in eq 5 B' is a constant containing the energy separations and extinction coefficients of states that are mixed, $c^*_{r\mu k}$ and $c_{s\nu k}$ are mixing coefficients for the heavy atom in the system, and ζ is the effective spin–orbit coupling constant).

The validity of eq 5 for these metal complexes could be determined if the energies of mixing states and the integrated intensities of these bands were accurately known. Unfortunately these experimental quantities and the mixing coefficients are generally not available. However, the analysis used by McGlynn[30] comparing the ratios of k_p, k_n, and ζ^2 for complex and free ligand is quite appropriate. For these complexes, only k_n and k_p for the Rh(dip)$_3{}^{3+}$ are proportional to ζ^2.[17] For the Ir(III) and Ru(II) complexes, the ratios of k_p and k_n are larger than predicted by a simple ζ^2 proportionality but are proportional to each other, apparently due to the enhanced d-orbital mixing in these complexes.

A luminescence polarization[31] study of Ru(dip)$_3{}^{2+}$ does corroborate the spin–orbit intensity mechanism for these *delocalized orbital* emitters. In all cases, an appropriate model for the variation of the k_n must involve the spin–orbit mixing as a dominant if not the sole contribution.

The emission of the *localized orbital* emitters (Table II) is within the O_h symmetry approximation and the Russell–Saunders limit assigned as ${}^3T_1 \rightarrow {}^1A_1$.

The only reported fluorescence from *localized orbital* d^6 complexes is that of the bis(diphenylphosphino)ethane (dppe) complexes of Ru(II) and Os(II).[32] This structured emission, overlapping the absorption, is anomalous and has been contradicted by luminescence data obtained for the (dppe)$_2$ complexes of Ru(II), Rh(III), and Ir(III).[33] The Ru(II) complex does not emit, but the Rh(III) and Ir(III)

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complexes give the characteristic structureless, broad-band emission with a large Stokes shift expected for *localized orbital* phosphorescence.

Acquisition of quantum yield data for d^6 *localized orbital* emitters is difficult because of the small quantum yields and the red or near-ir emission. Quantum yields (Table IV) are generally small (with the exception of some iodine- and bromine-substituted complexes[34]) and lifetimes are short, dominated by nonradiative processes, *i.e.*, $(\tau_p \approx 1/k_n)$.

The radiative and nonradiative rate constants for some nitrogen ligand complexes have been calculated from eq 1 and 2 assuming $\Phi_{isc} = 1$ and the results are tabulated in Table IV. Examination of these data (and the Φ_p data) for comparable Rh and Ir complexes (Rh(en)$_3^{3+}$ *vs.* Ir(en)$_3^{3+}$ etc.) indicates that the rate constants are not correlated with the spin–orbit coupling as in the case of *delocalized orbital* complexes nor does the increased spin–orbit mixing (Ir >Rh) result in enhanced luminescence yield. Indeed, the reverse effect is observed, *i.e.*, $\Phi_{Ir} < \Phi_{Rh}$ in general. While the k_p essentially obeys the McClure ζ^2 relationships, k_n shows a greater than ζ^2 dependence.

For these d^6 complexes, the completeness of intersystem crossing cannot be assumed. As for d^3 complexes, the absence of fluorescence, the primary basis for this assumption, would be explained by a large value $(\geq 10^3)$ for k_{ic}/k_f of the spin-allowed transition.

Quantum yield measurements[17] for the complexes Rh(dip)$_2$Cl$_2^+$ and Rh(phen)$_2$Cl$_2^+$ indicate that excitation into ligand-localized states produces consistently higher quantum yields than for excitation into d–d states. Independent of these measurements Ohashi and coworkers[35] have done laser excitation studies of the emission rise and decay times of the Rh(dip)$_2$X$_2^+$ complexes with X = Br and Cl and concluded that the crossover to the triplet manifold is more efficient from the ligand-localized singlet than from the d–d singlet.

Some Generalizations. The following comments are valid for the localized orbital emitters. (1) Phosphorescence is the dominant form of emission, with some few Cr(III) complexes exhibiting fluorescence. (2) Intersystem crossing is large, but not complete, for many *localized orbital* complexes. (3) Quantum yields are generally small (with the exception of halogenated Rh(III) complexes); therefore, $k_n/k_p > 1.0$. The nonradiative constant, k_n, for d^6 complexes does not show a pure ζ^2 dependence. (4) The ratio of the nonradiative to the radiative rate constant is generally larger for the spin-allowed process than for the spin-forbidden process. (5) d^6 phosphorescence and d^3 fluorescence are broad and structureless and exhibit a large stokes Shift, while d^3 phosphorescence is narrow and structured and has a small or zero Stokes shift. These generalizations are appropriate to the *delocalized orbital* emitters. (1) Only phosphorescence is observed. (2) Intersystem crossing is complete. (3) Quantum yields are large, equal to or greater than those of the respective free ligands. The constants k_n and k_p exhibit approximately ζ^2 dependence. (4) Phosphorescence spectra are structured and show a small Stokes Shift.

Theory: Some Answers

Success of the theories of nonradiative transitions in rationalizing isotope effects, energy gap dependence selection rules, and Kasha's rules for π-electron systems has been indicated. Certainly, construction of an appropriate theoretical framework for the relaxation of excited states in transition-metal complexes must recognize these successes and, for economy of effort, begin with this basis. Assuming the density of levels in the acceptor manifold is substantial, eq 6 can be used.[19] ($J^k(m,n)$ is the electronic

$$V_{mr,ns} = \sum_k J^k(m,n)F^k(mr,ns) \qquad (6)$$

factor, $F^k(mr,ns)$ is the vibrational factor, and k is the index of the promoting vibrational mode. F^k contains the Franck–Condon factor. The rate constant, k_n, is proportional to $V_{mr,ns}{}^2$.)

At this time, the absence of accurate wave functions precludes calculation of the vibrational factor, and uncertainty as to the deactivation path hinders evaluation of the electronic factor. However, some estimation of the value of this approach and insight into directions of future research can be acquired by use of this theoretical framework.

The Electronic Factor, J^k. For the delocalized orbital emitters, the transitions of interest are $T_1 \rightsquigarrow S_0$ and $S_1 \rightsquigarrow T_1$, where T_1 is the emitting triplet and S_1 and S_0 are, respectively, the lowest excited singlet state and the ground singlet state. The absence of fluorescence suggests dominance of spin–orbit coupling in the $S_1 \rightsquigarrow T_1$ process. However, comparison of the quantum yields of free ligand and complex indicates that the phosphorescent quantum yield ($T_1 \rightsquigarrow S_0$) may not always be enhanced by the heavy metal ion. The $T_1 \rightsquigarrow S_0$ process is influenced by the spin–orbit factor, although the precise dependence upon ζ^2 cannot be determined in the absence of information concerning the degree of metal mixing. No significant Φ variation with wavelength occurs for the (dip)$_3$ and (phen)$_3$ complexes, implying that intersystem crossing occurs from the lowest singlet, consistent with the Kasha rule.

The electronic factor for the localized orbital $^3T_1 \rightsquigarrow {}^1A_1$ process (d^6 system) shows a greater than ζ^2 dependence, thereby implying that the electronic factor is proportional to some combination of spin–orbit and vibronic coupling. A possible rationale for this deviation from a simple spin–orbit dependence can be obtained by the classification of these displaced excited states (T_1 and S_1) as "strong coupled" surfaces.[14,15,17]

The electronic factor for the $^2E \rightsquigarrow {}^4A_2$ process in the d^3 chromium complexes should show a simple ζ^2 dependence since the $^4T_2$ and ^2E states are spin–orbit mixed. Indeed, k_p and k_n for the Cr–S complexes (large spin–orbit coupling) do increase proportionately; therefore the resultant quantum yield is similar in magnitude to that of other Cr complexes.

Quantum yield data for Cr–S chelates[17] and temperature-dependent lifetime and intensity data[23,24] for the tris(acetyacetonate) ((acac)$_3$) complex of Cr(III) indicate that $\Phi_{isc} < 1$ and that the $^4T_2 \rightsquigarrow {}^2E$

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[34] J. N. Demas and G. A. Crosby, *J. Amer. Chem. Soc.*, 92, 7662 (1970).

[35] Y. Ohashi, K. Yoshihora, and S. Nagakura, *J. Mol. Spectrosc.*, 38, 43 (1971).

process is incomplete. Similarly, for d^6 *localized orbital* complexes, the dependence of Φ_p[17] and τ_p[35] upon excitation wavelength suggests that internal conversion is competitive with intersystem crossing.

Vibrational Factor, F^k. As suggested earlier, an appropriate vibrational factor should indicate the type of vibration and the mode of deactivation utilized to relax the excited state. The basic theory identifies two classes of vibrations: (1) promoter modes and (2) acceptor modes (vibrations involved in the overlap integral). Typically, acceptor vibrations are deemed most important to nonradiative efficiencies with a consequent neglect of promoter modes.

The Jortner–Freed[14,15] modification of the theory identifies the strong coupled limit as that in which the coupling strength, G, $\gg 1$, while the weak coupled limit is appropriate when $G \lesssim 1$. For the weak coupled limit

$$\langle\omega\rangle \gtrsim (1/2)\Delta S \qquad (7)$$

and for the strong coupled limit

$$\langle\omega\rangle << (1/2)\Delta S \qquad (8)$$

where ΔS is the measured Stokes shift and $\langle\omega\rangle$ is a mean acceptor vibrational frequency. Theory and experiment identify $\langle\omega\rangle$ for weak coupled systems as the maximum frequency vibration, thereby implying that a deuterium isotope effect should be observed where a hydrogen vibration is acting as an acceptor mode. The $\langle\omega\rangle$ for strong coupled vibration is expected to be an average (and from eq 8 would be a low frequency). Therefore, a strong coupled complex would not exhibit a large isotope effect, but would have a transition determined by some activation energy, E_A (Figure 1).

A small Stokes shift (vertical potential surfaces) necessitates weak coupling of the emitting and the ground state and requires a high-frequency (light atom) vibrational mode as the acceptor mode. But a large Stokes shift (displaced surfaces, Figure 1) may indicate strong coupling of the states, thus enabling utilization of low-frequency heavy-atom vibrational modes as the acceptor modes.

The small Stokes shift and the general similarity of the chelate emission to the free ligand imply that the d^6 *delocalized orbital* emitters can be classified as weak coupled emitters, although no experimental verification (isotope effect, temperature dependence or τ, Φ) is yet available.

The larger Stokes shift found for most *localized orbital* d^6 complexes is suggestive of a strong coupling (Table I). Indeed, if $\langle\omega\rangle \sim 300$ cm^{-1}, a metal–ligand atom vibration, the fundamental criterion is met. The inverse correlation of Φ with the magnitude of the Stokes shift for pairs of Rh(III) and Ir(III) complexes[5,6,17,33] is suggestive of the strong coupled limit. Generally, the Ir(III) complex has a smaller Φ_p (larger Stokes shift) than the Rh(III) complex. In all pairs of complexes the number and types of vibrations are constant and the triplet–singlet energy gap is approximately constant. However, no isotope data are available for these complexes to verify the use of the low-frequency vibrations as acceptor modes. Recent isotope studies[36] of τ and Φ_p for a series of *localized orbital* complexes of hexaammine- and halopentaamminerhodium(III) have been interpreted as indicating that these complexes are weak coupled emitters. However, lifetime measurements for *partially* deuterated hydrocarbons indicate that C–H bending vibrations can act as promoter modes.[37-39] Moreover, Robbins and Thomson[19] interpret absorption studies of deuterated $Cr(NH_3)_6{}^{3+}$ as indicative of a promoter mode function for N–H vibrations.

Although the evidence above for strong-coupled d^6 emitters is not conclusive, certainly the value of the Jortner–Freed model in identifying the pertinent acceptor modes is obvious. For example, the possibility exists that d^6 localized orbital complexes having light atom vibrational modes in close physical proximity to the metal ligand atom (N–H stretch in $Rh(NH_3)_6{}^{3+}$) might use the highest frequency modes as acceptor modes. Alternatively d^6 localized orbital complexes having no light atom modes (as the $M(dtp)_3$ and $M(dtc)_3$) close to the metal ion chromophore would necessitate use of low-frequency metal modes as acceptor modes.

Efficient nonradiative deactivation of the excited states of Cr(III) complexes is unexpected since the $^2E \rightsquigarrow {}^4A_2$ transition occurs between two weak coupled states (Table I) both localized on the heavy metal ion, necessitating use of high-frequency modes (ligand modes) as acceptor modes. However, the $^4T_2 \rightsquigarrow {}^2E$ process is apparently not complete; therefore the strong coupled $^4T_2 \rightsquigarrow {}^4A_2$ process may permit efficient utilization of low-energy metal–ligand vibrations *via* this alternative path. In addition, the high-resolution emission spectrum ($^2E \rightarrow {}^4A_2$) available for the Cr(exan)$_3$ complex indicates that ligand ring-bending mode (C_1–O–C_2) is coupled to the $^2E \rightarrow {}^4A_2$ electronic transition. Such coupling would permit use of high-energy C–H acceptor modes as required for a weak-coupled emitter, thereby permitting efficient nonradiative relaxation of the ^2E state. Finally, Robbins and Thomson[19] have pointed out that the linear correlation of k_n with the number of H atoms for a number of Cr(III) β-diketone complexes[20] implies that the highest energy vibrational mode (C–H, N–H, etc.) may be a promoter mode rather than an acceptor mode. Whatever the exact contribution of the high-energy vibrations, of most importance is the recognition in experiment and the concurrence by theory of the significance of internal ligand modes to the deactivation of metal localized transitions.

Toward a More Efficient Emitter?

The previous analysis permits an efficient luminescent complex to be described. The primary effect of the electronic factor is apparently diversion of energy from one manifold of states to another (*i.e.*, singlet to triplet) and/or the equal enhancement of existing radiative and nonradiative channels; therefore no unique electronic properties other than the existence of a lowest excited state in a detectable region

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(36) T. R. Thomas, R. J. Watts, and G. A. Crosby, *J. Chem. Phys.*, **59**, 2123 (1973).

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of the spectrum ($\lambda_{em} \lesssim 1100$ nm) appear necessary. The vibrational characteristics are more restrictive: (1) the ideal emitter should have only weak coupled excited states at lowest energy, that is, the lowest excited state should be a state with bonding character comparable to the ground state, and (2) the complex should be a species having no high-energy (C–H, N–H, etc.) vibrations coupled to the chromophoric unit. Such criteria are most likely to be met for d^3 ($^4A_2$ ground state) and d^5 ($^6A_1$ ground state) complexes. Coupling of high-energy ligand modes to the Cr^{3+} can occur, and the strong-coupled $^4T_2$ state can provide an additional nonradiative pathway if intersystem crossing is not complete; therefore, most d^3 complexes are not efficient emitters. Although Mn^{2+} luminescence is known, no quantum yields are available, the experiments being complicated by the lability of these complexes.

Generally, a lowest excited state produced by a $t_2 \rightarrow e$ type transition would not be expected to emit efficiently since such displaced surfaces can be *strong coupled* to the ground state, permitting efficient utilization of low-frequency vibrations. The absence of emission for d^1, d^7, d^8, and d^9 complexes, and for most d^6 complexes, is consistent with the existence in these complexes of low-lying d–d states.

Onward and Upward?

Some predictions pertinent to relaxation of electronic states of metal complexes can now be made from available emission spectra. Additional quantum yield data can be useful, although it is apparent that attempts to vary a single factor in the emission efficiency (by structural variation), while holding all other factors constant, is difficult.[17,19,21] The use of the optical photoselection technique to determine emission polarization for *delocalized orbital* emitters[31] is useful, but is likely of less use for *localized orbital* d^3 or d^6 complexes (in part because of intensity limitations). Temperature-dependent emission and lifetime data of partially and totally deuterated localized orbital complexes may provide further verification of the validity of the vibrational coupling model.

Theoretical studies will be hampered by the absence of accurate vibronic wave functions for these complexes, but high-resolution spectral data may permit experimental evaluation of vibrational overlap integrals for correlation with nonradiative rate constants.

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Protein Inhibitors of Proteolytic Enzymes

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The importance of protein–protein interactions in biological processes is widely recognized. Antigen–antibody interactions, interactions between enzyme subunits, the self-assembly of viral particles, and the interaction of proteolytic enzymes with their protein inhibitors are examples of important protein–protein interactions currently under active investigation. As a result of the great interest in serine proteinases, studies of the latter have progressed to a very detailed stage. Recent X-ray diffraction studies, for the first time, allow examination of such complexes at an atomic level. The nature and mechanism of this inhibition will be the focus of this Account.

Proteins with the ability to inhibit proteolytic enzymes have been isolated from a wide variety of plant and animal tissues. Some have been shown to be involved in the regulation of biologically important proteolytic processes (*e.g.*, blood clotting, digestion, sperm capacitation) and others have been related to important pathological conditions (*e.g.*, pul-

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