MASTER

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THE LUMINESCENCE OF METAL COMPLEXES

by

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Summary of Research Activities

This project has been aimed at determining the effect of structure and environment on the radiative and non-radiative transition probabilities in metal complexes. The increasing technological importance of luminescent materials serves to focus attention on the desirability of basic studies in this area. Ideally, the synthetic chemist could select in advance a compound with the desired luminescence properties and proceed to prepare it. While this ideal situation is not yet attained, it is clear that fundamental luminescence studies have already provided a guiding framework in which the search for a desired material is much more efficient. Witness the recent success in producing a liquid laser with a solution of a rare-earth complex.

The metal complexes form a group which is especially suitable for studying the effect of structure on transition probabilities. The possibility of varying the metal ion and the ligands over a wide range provides a systematic method of assessing the relevant factors. In many complexes the interaction between metal and ligands is so small that a perturbation approximation is useful. Within this approximation, electronic transitions may be classified as: (i) Metal localized, perturbed by the

ligands; (ii) Ligand localized, perturbed by the metal; and (iii) Charge transfer, ligand to metal or metal to ligand.

The fate of an absorbed light quantum may be described in a simplified fashion by reference to the following scheme:

In general, light is absorbed in a spin-allowed transition. The initially excited state may then relax to the ground state radiatively (k_2) or non-radiatively (k_3) or to a state of different spin-multiplicity (k_4) from which return to the ground proceeds radiatively (k_5) or non-radiatively (k_6). If the transitions are all ligand localized then A and B usually represent singlet states while C is a triplet. If the transitions are metal

localized, say on Cr(III), then A and B are the quartet states, 4A_2 and 4T_2 , and C is 2E .

In many cases, the absorption takes place in the ligand and is followed by intramolecular energy transfer to the metal. In this event more levels must be included but the basic description will be unchanged.

Thus, the evaluation of k_2 -- k_6 as a function of structure and environment has been the focal point of these studies. Information about the radiative transitions, k_2 and k_5 may be obtained from absorption spectra, although the spin-forbidden transitions denoted by k_5 are often weak and unresolved from the stronger spin-allowed bands in an absorption spectrum. Only through luminescence studies can the non-radiative transition probabilities, k_3 , k_4 , and k_6 , be studied. The prime data obtainable are luminescence quantum efficiencies, (Φ), and lifetimes, (τ), of fluorescence and phosphorescence. These quantities may be expressed in terms of the 1st order rate constants.

$$(1) \quad \Phi_F = \frac{k_2}{k_2 + k_3 + k_4}$$

$$(2) \quad \tau_F = \frac{1}{k_2 + k_3 + k_4}$$

$$(3) \quad \phi_P = \frac{k_4}{k_2+k_3+k_4} \frac{k_5}{k_5+k_6}$$

$$(4) \quad \tau_P = \frac{1}{k_5+k_6}$$

It is apparent that four data are insufficient to evaluate six unknowns. It is also true, unfortunately, that in many cases either fluorescence or phosphorescence are absent (too weak to measure). While the long-lived τ_P ($>10^{-5}$ sec) is easily measured, the short-lived τ_F (10^{-8} - 10^{-9} sec) is only measured with great difficulty, although an increasing number of laboratories are now equipped to measure nanosecond lifetimes.

In principle, the radiative rate constants can be evaluated from absorption spectral intensity, and it would appear that the four data are now adequate for the computation of the remaining three unknowns. Two problems arise in this connection. In the first place, when the ground and excited state geometries are not the same, k_2 and k_5 as measured from the absorption spectrum will not be the appropriate values to employ in equations (1) - (4). Secondly, accurate evaluation of spin-forbidden absorption intensities is often very difficult. The evaluation of k_5 for Cr(III) complexes has been one of the problems encompassed by this project.

The transition metal complexes are very suitable for the study of metal localized transitions. In these complexes the metal transitions are often at rather low energy and hence are not overlapped by ligand transitions. The d-d transition energies are dependent on ligand (in crystal field language, the parameter Dq varies with ligand) and a vast array of transition metal coordination compounds have been prepared. Cr(III) complexes were an obvious choice for initiating the study since the ruby luminescence was well known and in the 1930's many emission spectra of solids containing Cr(III) had been obtained. The great stability of these complexes in solution was also a favorable portent.

It was expected that the long-lived ${}^2E \rightarrow {}^4A_2$ emission would be most intense at low temperature and the common solvent EPA was chosen as a glass-forming environment. This was fortunate because only non-ionic complexes are soluble in this glass and chromium acetylacetonate was the complex selected for the initial study. Emission was then observed near $8000 \text{ \AA}$ rather than the expected $7000 \text{ \AA}$. This was surprising at first because the ${}^2E \rightarrow {}^4A_2$ transition energy is not dependent on Dq in the simple crystal field model and the transition was initially assigned as spin-allowed, ${}^4E \rightarrow {}^4A_2$. The long

emission lifetime ($>400 \mu\text{sec}$) was then determined and it was clear that a "nephelauxetic effect" was operative and that covalency effects were involved. A correlation was then suggested which has been validated in succeeding years, viz., ligands with π -bonding electrons reduce the ${}^2E \rightarrow {}^4A_2$ energy.

The lifetime, τ_p , was found to vary considerably as the substituent on the basic diketone ligand structure was altered. Thus, when the methyl groups on the periphery of the acetylacetonate anion were replaced by hydrogen atoms the lifetime was reduced from 420 to 40 μsec . This large effect can be attributed to an increase in the non-radiative transition probability, k_6 , an effect which is paralleled when naphthalene is deuterated. The deuterium isotope effect has been explained by current theories of radiationless transitions. However, a similar reduction of lifetime occurs when the methyl groups are replaced by more massive phenyl substituents. It is evident that non-radiative transitions are not to be explained simply in terms of a "mass effect".

In a number of complexes, the spin-forbidden absorption is sufficiently well resolved from the spin-allowed bands that the oscillator strength $f({}^2E \leftarrow {}^4A_2)$ can be evaluated. The geometries of the upper and lower states should be very similar since both states arise from the same electronic configuration, t_2^3 . Some uncertainty

is still involved because another spin-forbidden transition ${}^2T_1 \leftarrow {}^4A_2$ lies in the same spectral region as ${}^2E \leftarrow {}^4A_2$. From first-order perturbation theory, k_5 may be computed, but the reliability of such an approach is in doubt. In a number of cases, however, k_5 computed from the absorption spectrum and perturbation theory are nearly the same. Some confidence may be placed in values of k_5 when this concordance is obtained.

In any event, for many complexes $k_5 \ll k_6$ and consequently $\tau_p^{-1} \approx k_6$. Measured values of k_6 obtained in this manner vary from approximately zero to greater than $50 \times 10^3 \text{ sec}^{-1}$. As yet no reasonable correlation between structure and k_6 has been found.

From the relation

$$(5) \quad \frac{\phi_p}{\tau_p} = \frac{k_4 k_5}{k_2 + k_3 + k_4} = k_5 \phi_C({}^4T_2 \rightarrow {}^2E)$$

the efficiency of populating 2E may be estimated. This efficiency, which approaches unity for ruby, is often low [0.05 for $\text{Cr}(\text{CN})_6$]. There appears to be some relationship between π -bonding ligands and reduction in $\phi_C({}^4T_2 \rightarrow {}^2E)$.

Further support for the belief that ϕ_C is often smaller than unity comes from a study of the temperature dependence of k_6 in chromium acetylacetonate and several of its derivatives. In this work dilute mixed crystals in the corresponding aluminum acetylacetonate were

employed to separate purely thermal from viscosity effects. Two thermal quenching processes were observed, one with an activation energy of 7-8 kcal/mole, which corresponds with the ${}^4T_2 - {}^2E$ energy separation. Thus, back transfer from 2E to 4T_2 results in return to the ground state non-radiatively. Of additional interest in this connection is the computation of a preexponential factor of 10^{11}sec^{-1} , very large for a spin-forbidden non-radiative process.

In several cases Cr^{3+} systems, ruby and emerald, the ${}^2E \rightarrow {}^4A_2$ emission is quenched as the temperature is increased and ${}^4T_2 \rightarrow {}^4A_2$ fluorescence is activated. The "activation energy" for this process corresponds to the ${}^4T_2 - {}^2E$ energy gap. An analogous situation exists for $\text{Cr}^{3+}:\text{AlCl}_3 \cdot 6\text{D}_2\text{O}$ and $\text{Cr}^{3+}:\text{GASH}$ and it may be concluded that the thermal quenching of 2E generally proceeds via the 4T_2 state. In some cases, viz., $\text{Cr}^{3+}:\text{Al}(\text{acac})_3$ and $\text{Cr}^{3+}:\text{NaMgAl}(\text{ox})_3 \cdot 9\text{H}_2\text{O}$, no thermally activated ${}^4T_2 \rightarrow {}^4A_2$ emission is detectable and some uncertainty about the quenching pathway exists. An interesting system is $\text{Cr}^{3+}:\text{K}_3\text{Co}(\text{CN})_6$ wherein the lifetime of the 2E state decreases with temperature, while the luminescence yield remains constant. This can be ascribed to as thermally enhanced radiative transition probability k_5 .

One final point will illustrate the formidable task which confronts the experimentalist who wishes to use the ligand field scheme to interpret his results. The trix-oxalato chromium(III) anion can be isomorphously diluted in $[\text{NaMgAl}(\text{C}_2\text{O}_4)_3] \cdot 9\text{H}_2\text{O}$. This material crystallizes in two modifications, hexagonal and rhombohedral. The ^2E state splitting, due to combined spin-orbit and trigonal field interactions is 20 cm^{-1} in the hexagonal crystal but $>1 \text{ cm}^{-1}$ in the rhombohedral crystal. This indicates that the trigonal field is removed by packing distortion in the rhombohedral crystal, i.e. the environment is effectively cubic. In a cubic environment $^2\text{E} \rightarrow ^4\text{A}_2$ is magnetic dipole allowed but electric dipole forbidden and should have a longer lifetime than the electric dipole allowed transition in the trigonal environment. Yet, the lifetimes of both systems are nearly the same while in the analogous case, $\text{Al}_2\text{O}_3:\text{Cr}^{+3}$ and $\text{MgO}:\text{Cr}^{+3}$, the lifetimes differ by a factor of 10.

Although the major portion of the work during the contract period has been involved with Cr^{3+} complexes, a study of ligand-localized emission in transition metal oxinates was completed.

In addition the experimental studies described above, a substantial effort was devoted to the calculation of electronic structures of ligands with π -electron systems.

In summary, we have amassed a substantial body of information pertaining to the depopulation of the 2E state in Cr^{3+} systems. Some of the factors involved in the quenching processes have been identified but a detailed understanding is still lacking. Details of the work are contained in publications listed in the following bibliography.

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Training Provided by Contract

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