

Inversion of Excited States of Transition-Metal Complexes

Abstract. *The nature of the emission from central metal ions in complexes can be controlled by chemical alteration of the ligands. For iridium(III) species three types of emission have been observed, each originating from a different and orbitally identifiable excited state. Principles useful for designing new luminescent materials are formulated. They can be used for guiding photochemical research and for designing new analytical methods.*

Investigations of the spectroscopic properties of transition-metal complexes have led to the classification of the natures of their low-lying excited states. For d^6 systems that contain π -conjugated ligands, and which have been investigated with some degree of completeness, the excited levels responsible for the luminescences can be classified into three convenient categories: (i) $d-d$ excited states in which an electron on the metal ion has been promoted from an essentially nonbinding d orbital (t_{2g} in O_h) to a higher one (e_g in O_h), (ii) $d-\pi^*$, or charge-transfer (CT), excited states in which an electron has been promoted from a d orbital of the metal ion to an antibonding π orbital associated with the ligands (1), and (iii) $\pi-\pi^*$ excited states in which an electron in a bonding molecular orbital derived from the ligand π system has been promoted to an antibonding π orbital also essentially located on the ligands.

It is of considerable theoretical and experimental interest to designate the orbital labels of the lowest-lying excited states in complexes. Since the first excited level in a complex is, except in rare cases, the one from which luminescence occurs, the spectroscopic properties of the observed photoluminescence bands provide criteria for assigning the orbital labels at least to the lowest-lying excited state.

Luminescence arising from a $d-d$ excited state appears as a gaussian-shaped emission band that is devoid of structure and is not displaced significantly as the nature of the glass or even the physical state of the material is changed. Decay times range from ~ 10 to $500 \mu\text{sec}$. Typical of this class are emission from potassium hexacyanocobaltate(III) (2) and dichlorobis(2,2'-bipyridine)rhodium(III) chloride (3). For complexes for which quantum yields are available, radiative lifetimes are on the order of 10 to $1000 \mu\text{sec}$.

Luminescence from a CT excited state is almost always highly structured (at 77°K) with a prominent vibrational progression, is fairly intense, and decays, at least at 77°K , with a lifetime

on the order of a few microseconds. The bands are shifted substantially by a change of the physical state or the composition of the matrix in cases where the complex has a significant dipole moment. The well-studied emission from the tris(2,2'-bipyridine)ruthenium(II) cation is a superb example of this type (4). Radiative lifetimes at 77°K are ~ 10 to $100 \mu\text{sec}$.

The final category, luminescence originating from a $\pi-\pi^*$ excited state, such as that observed from the tris(2,2'-bipyridine)rhodium(III) and tris(1,10-phenanthroline)rhodium(III) cations, has its own set of classifying properties. Such emissions decay in relatively long times (on the order of millisec-

onds), and the transitions lie at energies comparable to those observed for the solvated free ligands. The structures of the luminescence bands also resemble the structures of the bands observed for the solvated ligands (3).

For many d^6 complexes the emission characteristics are uniquely dictated by the orbital nature of the luminescing state; conversely, one can use the observed properties of the electronic emission band to classify the orbital characteristics of the lowest-lying excited state of a new molecule. When designing luminescent materials one can, by a judicious choice of metal ion and ligands, determine the orbital nature of the first excited state and, hence, prescribe a specific type of emission. For example, to obtain $d-d$ luminescence one must choose a metal ion and a set of ligands such that a low value of Δ , the crystal-field splitting parameter (5), can be achieved and a $d-d$ excited state will be lower than any $d-\pi^*$ or $\pi-\pi^*$ states in the molecule. If one wants a CT emission, it is neces-

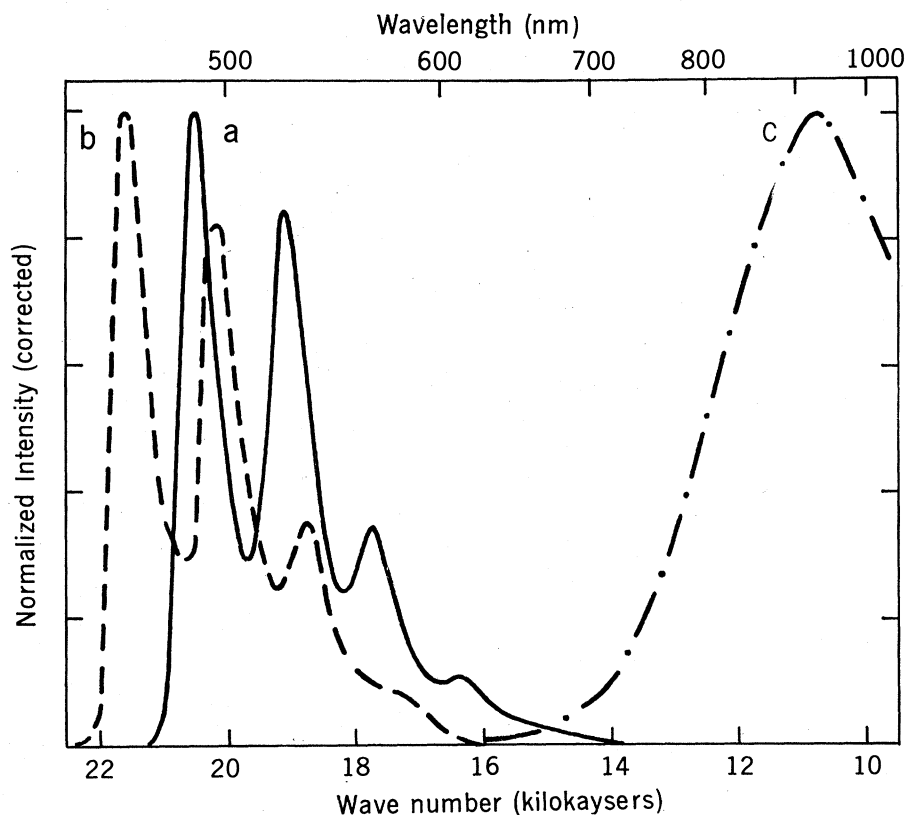


Fig. 1. Luminescence spectra of three iridium(III) complexes containing 1,10-phenanthroline as part of the ligand system. Curve a, dichlorobis(5,6-dimethyl-1,10-phenanthroline)iridium(III) chloride in water-methanol glass (1 : 4, by volume) at 77°K ; mean decay time, $190 \pm 5 \mu\text{sec}$. Curve b, *cis*-dichlorobis(1,10-phenanthroline)iridium(III) chloride in water-methanol glass (1 : 4, by volume) at 77°K ; mean decay time, $6.92 \pm 0.05 \mu\text{sec}$. Curve c, solid potassium tetrachloro(1,10-phenanthroline)iridate(III) at 77°K ; the low energy and intensity of the emission precluded any measurement of the decay time.

sary to choose an ion, such as ruthenium(II), whose Δ is high but whose oxidation potential is sufficiently low such that a $d-\pi^*$ state becomes the lowest excited state in the molecule. Finally, to obtain $\pi-\pi^*$ emission one must select a system with a substantial crystal-field splitting (in order to keep the $d-d$ levels high in energy) and with an oxidation potential of the central ion that is high enough to prevent a $d-\pi^*$ state from becoming the first excited configuration. The lowest excited state in the molecule then becomes $\pi-\pi^*$ in nature, and the characteristic $\pi-\pi^*$ emission appears.

Although in the past all three types of emission have been observed from molecules containing ions with a d^6 configuration, it has been necessary to change the central metal ion in order to obtain the oxidation potentials and ligand-field splittings necessary for a proper disposition of the excited levels. Recently, however, we have been able to obtain a $d-d$, a CT, or a $\pi-\pi^*$ emission from complexes of the same metal ion, iridium(III), by a chemical modification of its ligand environment.

In Fig. 1 we have plotted the absorption and luminescence spectra of three different iridium complexes, all containing *o*-phenanthroline or substituted *o*-phenanthroline as part of the ligand system. In each molecule the iridium ion feels a potential dictated by the total ligand environment. Excitation of any of the three species at 77°K in a glass results in a luminescence which has been plotted in Fig. 1. We see that the photoluminescence observed from these three molecules is radically different in nature. In curve a the luminescence has structure and decays with a measured mean life of $190 \pm 5 \mu\text{sec}$. This luminescence occurs in a region of the spectrum that is very close to the emission from the 5,6-dimethyl-1,10-phenanthroline molecule itself, and we assign it to a $\pi-\pi^*$ emission. The slight red shift ($\sim 400 \text{ cm}^{-1}$) from the luminescence of the solvated ligand is due to the perturbation of the $\pi-\pi^*$ state by interaction with $d-\pi^*$ states and the metal ion. In curve b the emission has a prominent vibrational progression and decays in $6.92 \pm 0.05 \mu\text{sec}$ at 77°K. A quantum-yield measurement shows the radiative life to be $\sim 14 \mu\text{sec}$ (6). These properties are characteristic of the emission observed from complexes of ruthenium(II) at 77°K; the latter are known to be CT

transitions. We thus believe that the lowest excited state in this iridium(III) molecule is $d-\pi^*$ in nature. Curve c shows the emission from the tetrachloro(1,10-phenanthroline)iridium(III) complex ion. Here the observed luminescence band is broad, structureless, almost gaussian in shape, an indication that the emission originates at an excited $d-d$ level.

Figure 1 demonstrates that it is possible to change the nature of the low-lying excited states of the complexes of the same metal ion in the same oxidation state from $\pi-\pi^*$ to $d-\pi^*$ to $d-d$ by a suitable chemical modification of the environment of the central species. We have also achieved $\pi-\pi^*$ emission from the porphyrin and dibenzoylmethide complexes of iridium(III) and $d-d$ emission from several iridium(III) species containing pyridine and halides as ligands.

The present study shows that it is possible to design luminescent materials of a single metal ion that have predetermined optical properties. By a proper choice of ligands and chemical structures one can "tune" the frequency and characteristics of the emitted light. There is every reason to believe that this kind of molecular design can be carried out for many other ions to yield a host of luminescent materials having varied but selected optical properties.

A second implication of this work lies in the field of photochemistry. Since the lowest-lying excited states certainly must be involved in some of the photochemical reactions that inorganic complexes undergo, these results demonstrate that it is possible to design molecules containing the same metal ion

in which the lowest-lying excited states are substantially different in nature. One may then be able to use such molecules as photochemical energy donors or even possibly as subjects for the study of the photochemistry of inorganic materials.

A further area of research that could be guided by these principles is the field of analysis by fluorescence or phosphorescence. The results presented here establish guidelines for developing new sensitive luminescent indicators.

Finally, the demonstration above clearly shows the efficacy of using several spectroscopic parameters, such as mean decay time, quantum yield, and band structure as diagnostic tools for assigning the orbital natures of the excited states of complexes. For many molecules the results are far less ambiguous than assignments based on absorption spectroscopy alone.

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References and Notes

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7. Research supported by the Air Force Office of Scientific Research, AFOSR(SRC)-OAR, USAF grant 68-1342.

6 August 1970; revised 6 October 1970

How Did Venus Lose Its Angular Momentum?

Abstract. *Venus now has a retrograde and negligible spin, but it very likely started with a typical planetary spin: prograde and with a 10- to 20-hour period. The usually assumed mechanism of solar tidal friction is quite insufficient to remove this angular momentum. Instead, we postulate capture of a moonlike object from an initially retrograde orbit: it would despin Venus and suddenly transform the planet's rotational kinetic energy into internal heat, which would lead to volcanism and the liberation of large amounts of volatiles. The moon would disappear by crashing into the surface of Venus.*

The planet Venus occupies a quite anomalous position in the solar system by having a spin angular momentum that is clearly retrograde. Since the first radar measurements at the Jet Propulsion Laboratory in 1962 by Carpenter and Goldstein, it has be-

come apparent that Venus has a sidereal period of 243.09 ± 0.18 days; the rotation vector is retrograde and inclined by 1.2° from the normal to the orbit plane and by 2.2° from the normal to the ecliptic (1). All other objects in the solar system have ro-