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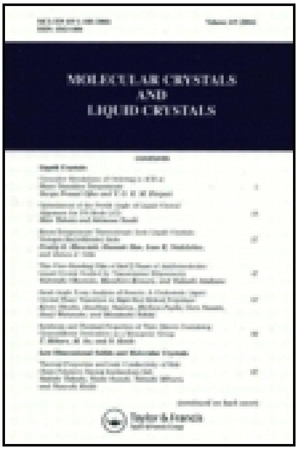

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Luminescent Organic Complexes of the Rare Earths

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Luminescent Organic Complexes of the Rare Earths†

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Contents

I. Introduction

In recent years the rapid advances in the understanding of the nature of chemical bonds and in the application of quantum mechanics to chemical problems have imparted a great impetus to

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studies of luminescent materials, studies which have been primarily directed toward the elucidation of the electronic structures of the molecules. Great strides have been made in the understanding of organic materials employing the complementary studies of absorption, fluorescence, and phosphorescence, the latter a comparatively recent development.[1]

The sophisticated theoretical methods currently available for studying the electronic structures of atoms and ions, coupled with the equally sophisticated, although mathematically more tedious, techniques now used for unraveling the electronic structures of organic molecules, provide the basis for an understanding of the electronic properties of complexes, compounds having metal ions coordinated with organic ligands. This class of complex compound is a hybrid lying between inorganic and organic materials and provides an especially interesting set of substances for the study of chemical bonding, of the perturbations of energy levels via interactions between organic ligands and metal ions, and of the migration of energy across the metal-organic bonds. Luminescence spectroscopy, complemented by absorption spectrophotometry, comes into its own here as an important, exceedingly fruitful, and fascinating method of investigating fundamental problems in these systems where the substances can be well characterized, are sufficiently simple for quantitative study, but are complicated enough to display interesting phenomena. A subclass of such compounds, luminescent coordination compounds containing organic ligands and having metal ions with unfilled 4f electronic shells, is the subject of this review.

II. Luminescence Originating from Intra-4f Transitions

The chemistry of the rare-earth elements has not been as extensively investigated as that of many other elements of the periodic table, perhaps because it is in many ways less interesting, since all the elements usually display a characteristic tervalence which accounts for the majority of their known compounds. The ions differentiate themselves, however, quite markedly by the possession of an unfilled 4f electronic shell which can hold up to fourteen electrons. Beginning with lanthanum having no 4f electrons and extending through lutetium having fourteen 4f electrons, these elements provide a fascinating series all displaying the same stable tervalent chemical oxidation state and yet having different numbers of electrons in the 4f shell. Chemical manifestations of the different numbers of 4f electrons in these ions are varied magnetic moments for the compounds, minor differences in ionic radii, subtle changes in the coordination spheres, and the appearance of unexpected oxidation states which can be achieved because of the unusual stability associated with a filled or half-filled 4f shell. Spectroscopically the ions are very interesting, since the similarity of the chemical properties among the ions provides a framework for detailed studies of the electronic characteristics contingent upon the number of electrons in the 4f shell. One of these characteristics, displaying the electronic differences of the various rare-earth ions magnificently, is the phenomenon of intramolecular energy transfer.

It was discovered by Weissman in 1942 that β-diketone coordination compounds of tervalent europium, terbium, and samarium exhibit unusual luminescence properties when excited by near ultraviolet light.[2] The compounds emit visible radiation characteristic of the rare-earth ions. Thus, intra-4f electronic transitions, which are known to originate from levels derived from the electrostatic and spin-orbit interactions among the 4f electrons *within* the rare-earth ions, occur whenever the excitation is carried out in the intense ligand absorption bands. These ligand bands (molar extinction coefficient $\sim 10^4 \sim 10^5$) are π–π^* in nature and are characteristic of the coordinated ligands *surrounding* the central chelated ions. Weissman realized that the energy was being pumped into the electronic system of the complex characterized by the π-electronic levels of the ligands and was subsequently migrating to the central chelated rare-earth ion, from whence characteristic luminescence (line emission) of the ion occurred. He designated this process *intramolecular energy transfer*.

The phenomenon was observed and studied subsequently by Sevchenko and coworkers[3] who reproduced some of the work of

Weissman and carried out investigations at various temperatures. Later Crosby and Kasha[4] extended the investigations to ytterbium complexes and demonstrated that intramolecular energy transfer could occur even when unusually large energy gaps existed between the excited singlet or triplet state of the complex and the level of the rare-earth ion from which the luminescence arose. In none of this work was the path of energy transfer, let alone the mechanism of energy transfer, understood in any detail.

A. PATHS OF ENERGY MIGRATION

A first step in the unraveling of the energy transfer process came with the work of Crosby *et al.*[5–7] They investigated a wide variety of β-diketonate chelates of the rare-earth ions and established a plausible path for energy migration in these systems. Using emission spectroscopy they obtained a quantitative measurement of the positions of the excited singlet, triplet, and rare-earth ion levels present in rare-earth chelates; then by correlating the relative positions of these levels with the observed luminescences, these investigators were able to establish an empirical rule for the occurrence of line-like emission from rare-earth chelates. Specifically they established that the requirement for the stimulation of rare-earth line emission from a given chelate is "*the lowest triplet-state energy level of a complex must be nearly equal to or must lie above the resonance energy level of the rare-earth ion*". In this context, *resonance energy level of the rare-earth ion* is defined as that level from which the line emission of the rare-earth ion originates. In Fig. 1 the energy levels of several rare-earth ions, along with the measured triplet-state levels of various complexes, are plotted. In every case where the measured triplet-state levels are nearly commensurate with or lie above a resonance level of a particular ion, emission from that ion level is observed whenever the compound is excited in the π—π^* absorption band characteristic of the organic part of the molecule.† Whenever a triplet state lies

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† For an account of the experimental techniques used to measure the positions of singlet and triplet levels in rare-earth chelates, as well as references to papers establishing the resonance levels, see Ref. 7.

decidedly below a resonance level of a given ion, then no emission from that ion level is observed.

An especially interesting case is that of the europium ion which exhibits two resonance levels, one at 17,257 cm^{-1} and a second at

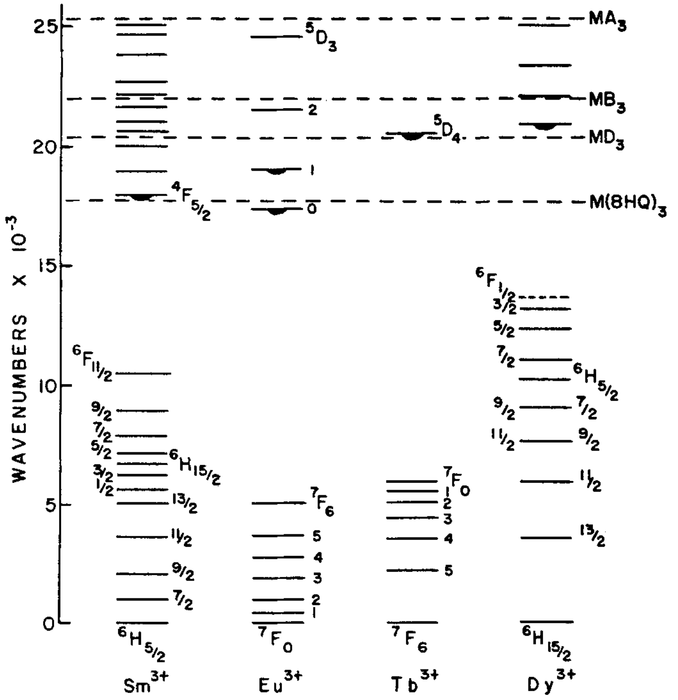

Figure 1. Energy level diagram for rare-earth chelates: (– – –) lowest triplet level for the complexes; (——) rare-earth ion level; (—▾—) rare-earth ion resonance level in chelates. Excited singlet states of the complexes have much higher energies and are not shown. Likewise only the lowest triplet-state energy for a complex is given. See Appendix for explanation of abbreviations. See Refs. 7, 15, 25 for discussions of radiationless processes.

19,020 cm^{-1} (see Fig. 1).[8] Whenever a chelate of europium with 8-hydroxyquinoline[7] or with *o*-hydroxybenzophenone[9] is excited by ultraviolet light in an absorption band characteristic of the organic part of the molecule, luminescence is observed only from the

$^5D_0$ level and none from the upper $^5D_1$ level. This observation was interpreted by Crosby *et al.*[7, 9] as proof that the energy traveled through the triplet manifold and then down to the $^5D_0$ and could not travel uphill to the $^5D_1$. Similar observations were made on thulium[10] and also on samarium[9] where the samarium ion luminescence was turned on or off by varying the number of ligands around the ion, thus raising and lowering the triplet-state energy level relative to the resonance energy level by means of ligand interactions.

This triplet-state energy-transfer pathway was subsequently assumed by other investigators in the study of chelates of the rare earths with different numbers of β-diketone ligands[11] and also with various different types of ligands.[12–14] As recently pointed out,[15] however, the observation of luminescence when the triplet state is above the resonance level is not absolute proof that it is the triplet manifold which contains the donor level for the transfer process. According to Kleinerman, energy could go directly from the singlet of the complex to the rare-earth ion followed by *back transfer* to the triplet state of the complex which would thus act as a quencher for the ion state. According to this view, in the case of europium a triplet level between $^5D_1$ and $^5D_0$ could drain off the energy from $^5D_1$ and therefore quench its luminescence, while the energy trapped in $^5D_0$ would provide the characteristic red europium lines which are observed. A detailed analysis of the experimental results provides no conclusive proof that such a singlet transfer path is ruled out. Indeed the observed weak phosphorescences which have lifetimes longer than the lime emissions[7, 16–19] indicate that transfer is not coming from the lowest triplet state. Such conclusions, however, are based on the assumption that the observed phosphorescences arise from the same species in which energy transfer is occurring. As pointed out by Bhaumik *et al.*[20] recently, the weak phosphorescences have structures and profiles which are very similar to, or identical with, those of the corresponding negative ligand ions, so the phosphorescences are probably traceable to dissociative species which are not involved in intramolecular energy transfer. Therefore the weak emissions probably have no bearing on the problem. These latter results weigh heavily in favor of triplet transfer.

To date three paths have been proposed for the energy transfer process by which the excitation energy absorbed in the π—π^* electronic bands of the ligands migrates to the resonance 4f electronic levels of the ions. They are:

I: [Singlet (S_1)] ⇝ [Triplet (T_1) or a triplet slightly higher than T_1] ⇝ [Rare earth ion (RE) level] → [Emission][7]
II: [Singlet (S_1)] ⇝ [Rare earth ion (RE) level] → [Emission][15]
III: [Singlet (S_1)] ⇝ [Rare earth ion (RE) levels higher than T_1] ⇝ [Triplet (T_1)] ⇝ [Rare earth ion (RE) levels lower than T_1] → [Emission][21]

An interesting attempt to decide among these possibilities was recently carried out by Bhaumik and El-Sayed.[21] By utilizing systems demonstrating *inter*molecular energy transfer in addition to *intra*molecular energy transfer, they cite experiments strongly supporting paths I and III involving the triplet state.

The weight of evidence in the literature[20–22] favors a pathway in which the energy migrates from the triplet manifold of the complex to the rare-earth ion levels (Paths I and III) and against a singlet transfer (Path II); however, there seems to be no *a priori* reason that singlet transfer could not occur, and there is no reason for believing that in some complexes, owing to the electronic structure of the organic ligand *vis-a-vis* the rare-earth ion, singlet transfer may be more important than triplet transfer.

B. Rate of Energy Transfer

In addition to the problem of the path of transfer, singlet or triplet, there is also the question of the rate of transfer. Studies on the rate have been made by Freeman and Crosby,[17] who set a lower limit of 5×10^5 sec^{-1} (limited by the instrument used) for the rate constant of energy transfer assuming a triplet mechanism, although this limit is just as valid for migration via a singlet path. A lower limit of 10^6 sec^{-1} was deduced by El-Sayed and Bhaumik[22] based on experiments involving *inter*molecular energy transfer between benzophenone as a donor and rare-earth chelates as acceptors in fluid solutions with oxygen acting as a quencher. This value agrees well with a lower limit of 10^7 sec^{-1} quoted by Kleinerman *et al.*[23] Later Bhaumik and El-Sayed raised their estimate to 10^9–10^{10} sec^{-1} arguing from quenching experiments, employing Stern-Volmer diagrams[24]†

If the energy migration after excitation is indeed from the singlet manifold of the complex directly to the resonance level of the rare-earth ion without involving the triplet levels, then transfer would have to compete with singlet-triplet intersystem crossing which is known to be on the order of 10^8 sec^{-1} in organic hydrocarbons[25] and is estimated to be $\sim 10^{11}$ sec^{-1} for complexes of rare-earth chelates.[24] If, as appears more probable, the mechanism is via the manifold of triplet levels, the present data indicate a rate faster than 10^9 sec^{-1}. The upper limit on the transfer would, of course, be 10^{12} to 10^{13} sec^{-1}, for it is impossible to visualize any reasonable mechanism faster than a vibrational relaxation which is of this order of magnitude. Such high rates of transfer make the original suggestion plausible[7, 10] that transfer in some complexes does not go via the *lowest* triplet but by some higher level, possibly a higher triplet or even an excited vibronic level built on the lowest one. Partial transfer from a higher triplet has again been suggested[14] to explain the simultaneous appearance of weak emission from the $^5D_4$ level of terbium along with organic phosphorescence originating from the lowest triplet of the complex.‡

C. MECHANISM OF TRANSFER

Contingent upon the path the energy takes in its migration from the electronic states localized on the organic part of the complex molecule on its way to the rare-earth ion is the question of the coupling enabling the transfer process. Until now no theoretical

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† In Ref. 24 the units are erroneously given as liter/mole per sec. They should be sec^{-1}. This error was corrected in Ref. 21. (Private communication from the authors.)

‡ An alternate explanation invoking direct excitation of the chelated ion seems more probable, however; the terbium ion has an intrinsic absorption in the region of excitation generally employed.[26]

investigations have appeared applying detailed quantum mechanical calculations to the problem. A vibronic coupling of the electronic states of the rare-earth ion with those of the organic part through an exchange mechanism while preserving the total spin of the molecule was suggested by Crosby *et al.*[7] Mixing of the $^5D_1$ and $^5D_0$ electronic states of the tervalent europium ion with the lowest triplet level of the complex via a spin-dependent mechanism was also mentioned by McAvoy *et al.*[14] A quantitative investigation has not yet appeared.

Indeed, the apparent insensitivity of the transfer efficiency to the symmetry of the ligands around the ion and even the number of ligands attached to the ion (*vide infra*) indicates that very loose electronic restrictions (i.e., conditions independent of the detailed geometry of the complexes and the exact character of the bonds) are operating. Until the exact path of transfer is securely nailed down, extensive calculations would probably be premature.

The present developing technology of very fast high-intensity flashes will probably lead to investigations on these problems. Low-temperature, high-resolution, experimental results on extremely well-purified and definitively characterized complexes having triplet levels at various positions with respect to resonance levels of the chelated ions are needed in order to throw light on the problems of the energy transfer efficiency, the path of the migration, and the factors influencing the transfer rate.

III. Bonding

Although both tris (sixfold) and tetrakis (eightfold) coordination have been well substantiated for the trivalent rare-earth ions, laser applications have led to more interest in the bonding properties of the tetrakis species. For a tris β-diketonate chelate the compound is neutral since the negatively charged β-diketone ligands just balance the central tripositive rare-earth ion. For a tetrakis species the four bidentate negative ligands form with the tripositive ion a negatively charged entity and some cation is required for charge balance. This ionic nature makes the tetrakis complexes more soluble in general than the analogous tris ones. In addition, the tetrakis complexes are evidently more stable than their tris analogs and therefore more amenable to experimental investigations.

For the lanthanide tervalent ions there are nine vacant orbitals for bonding. These are the five 5d, the one 6s, and the three 6p orbitals. That the 4f orbitals are only very slightly involved in bonding is shown by the relative insensitivity of the positions of the 4f energy levels to the immediate chemical environment,[7] and to a good approximation, these orbitals can be ignored in a discussion of the primary bonding in the complexes. The 5f orbitals are considerably higher in energy and, although possibly involved in the bonding, can be ignored as a first approximation.

According to Brecher *et al.*[27] there exist three electronic configurations of the central ion which can give rise to eightfold coordination, depending upon which of the nine available vacant orbitals are left out of consideration: d^5sp^2 in which the coordinating oxygens are arranged with the symmetry of a face-centred isosceles prism; d^5p^3 which produces an Archimedean antiprism; and d^4sp^3 which can yield either an antiprism or a tetragonal dodecahedron. These authors have discussed the bonding of the tetrakis complexes primarily in terms of the d^4sp^3 configuration, since their spectroscopic evidence points to this kind of structure. The remaining d orbital not involved in bonding is then vacant and available for additional coordination by an adduct. The easy assimilation of an adduct molecule such as dimethylformamide indicates that the ninth empty orbital is used in this way.

These same authors have also discussed the change in configuration which occurs when another entity such as a dimethylformamide molecule approaches the tetrakis anion in solution to form a new nine-coordinated entity, and they point out that only small energy and configurational changes are necessary in order to lower the symmetry and produce new spectroscopic species. They were able to discuss the bonding in tetrakis complexes and the changes in bonding which occur with addition of an adduct entirely in terms of σ-bonding through s, p, and d orbitals without invoking additional bond types. The discussion encompassed the eight- and ninefold coordinated species both in solution and in solids.

It was pointed out by Bauer *et al.*[28] that the variety of structures suggested by the fluorescence spectra of tetrakis chelates in different solid environments probably cannot be accounted for in terms of a conventional directed valence theory. These authors speculate that some admixture of π-orbital bonding from the quasiaromatic chelate rings to the lanthanide ion may be of significance in the complexes. Because of the availability of so many orbitals of not too different energies in a rare-earth ion and the number of vacant excited orbitals on the π-electronic systems surrounding the ion, this view is probably correct. Any quantitative evaluation of the amount of π-bonding appears at this stage, however, to be a very difficult problem.

The nature of the 4f orbitals, that is, the fact that their electronic density distribution is essentially localized inside the ion, allows these electronic states to be discussed separately from the primary bonding responsible for the thermodynamic stability of the complexes. This postulation of essential localization of the 4f electrons within the rare-earth ions is amply justified by the small splittings and frequency shifts observed for the intra-4f electronic transitions whenever the ligands are changed. A good starting point, therefore, for the discussion of the shifts in the energy levels due to the ligand environment is the free-ion spin-orbit states. Because of the high atomic number, J (the total angular momentum quantum number) is the only good quantum number in the free ion, and the proper symmetry-adapted wave functions for a given complex must be constructed from free-ion J-classified functions. These free-ion J states can then be thought of as perturbed by the surrounding ligands. Mixing, under the crystal field, of states having different J parentage, can be safely ignored, for the crystal-field splitting amounts to only $\sim 10\%$ of the spin-orbit coupling energy.

To calculate the resultant first-order splittings due to the surrounding ligands, two models are available. The first is the crystal-field model which assumes that the oxygens (or other heteroatoms) in a complex can be replaced by point charges of an undetermined magnitude arranged in a geometry dictated by the chemical and spectroscopic evidence. According to this model no leakage of 4f electrons over onto the ligands is put into the calculation, and the computed splittings arise entirely from Coulombic repulsions between the 4f electrons and the pseudo point charges which have replaced, conceptually, the coordinating oxygens (or other heteroatoms). A second model, proposed by Jørgensen *et al.*,[29] throws the entire burden of the splitting of the 4f electronic levels upon a small overlap between the 4f orbitals and the σ orbitals of the coordinated ligands.

The models described above have been tested quantitatively for tris complexes of ytterbium and thulium. Optical absorption and emission spectra of several tris β-diketonate chelates of trivalent ytterbium were measured and the experimental values of the ligand-field perturbed $^2F_{5/2}$ and $^2F_{7/2}$ levels of Yb^{3+} were compared with the splittings predicted by the electrostatic crystal-field model and a contact covalent model.[30] Good agreement between theory and experiment was obtained from the electrostatic crystal-field calculation and somewhat poorer agreement from the ligand-field covalent calculation. A reasonable estimate for the geometry of an ytterbium tris complex was also obtained by means of the procedure. From a quantitative fitting of the spectrum to the electrostatic model a charge of -0.82 electrons was calculated for each oxygen of the negative, coordinated dibenzoylmethide ion, a value which reflects the polarization of the carbon–oxygen bond in a complex owing to the proximity of the trivalent positive ion. This value agrees remarkably well with that calculated by Forster[31] for an acetylacetonate negative ion in which the electronegativity of the oxygen was deliberately overemphasized.

A similar calculation carried out on Tm^{3+} chelates[32] gives an edge to the electrostatic model for a better accounting of the splitting of the complete set of the terms belonging to the ion. The calculations for both Yb^{3+} and Tm^{3+} complexes did not, however, reveal any glaring inconsistency in either the electrostatic or the covalent, so-called σ-antibonding, model for the complexes. In both these calculations, of course, π-overlap was entirely ignored which seems reasonable in view of the small σ-overlap parameters needed in the covalent model to fit the observed spectra. No detailed calculations of the line splitting manifested by tetrakis chelates have appeared.

The very fact that energy transfer to 4f electronic levels occurs at all shows that some covalent bonding is present. The exact description of such bonding is a difficult problem, however, and the work quoted above[29] represents a first attempt in this direction. Additional evidence for involvement of the 4f electrons in covalent bonding is presented by Katzin and Barnett.[33] Even an attempt to explain rather unusual intensity variations for intra-4f electronic transitions as a function of ligand geometry and interactions has been presented.[34] More work along these lines obviously is needed in order to obtain accurate models for explaining the experimental splittings and intensities observed for rare-earth 4f electronic levels in complexes.

IV. The Chelate Laser

The ability of rare-earth chelates to absorb energy in a broad organic absorption band, to transfer this energy efficiently to the rare-earth ion, and finally to give it up as bright-line emission in a narrow wavelength region, makes these molecules obvious candidates for laser applications. Laser possibilities for these complexes were pointed out by Whan and Crosby[16] with reference to the trisbenzoylacetonate and trisdibenzoylmethide complexes of europium, samarium, and terbium. Laser possibilities were also pointed out by Bykov[35] who emphasized the versatility of such systems and envisioned a whole series of compounds possessing the desired properties. Their possible value for lasers was recognized also by Rieke and Allison.[36]

The molecular approach to lasers with special emphasis upon chelate systems was discussed by Lyons and Bhaumik[37] who detailed the advantages and disadvantages of the chelate approach to the laser problem. At the same time Ohlman *et al.*[38] reported investigations on europium trisdibenzoylmethide for possible laser applications and reported a detailed study of its excitation, absorption, and emission spectra, along with the quantum efficiencies and fluorescent decay times of the principal emission lines as functions of temperature and solvent.

The exceptional appeal of plastic hosts for laser compounds, materials which could be easily machined and fabricated to specification was mentioned by Filipescu *et al.*[39] who reported preliminary studies of the fluorescences of rare-earth chelates in vinyl hosts with emphasis upon the samarium ion, an unfortunate choice, as it turned out. The design of lasers based on rare-earth chelates was also considered by Schimitschek and Schwarz[40] who presented a numerical evaluation of the problem using europium salicylaldehyde as an example. These authors came up with a surprisingly low predicted energy threshold, quantitatively demonstrating the feasibility of chelate lasers. Fluorescence decay times of rare-earth chelates were reported by Rieke and Allison,[36] Bhaumik *et al.*,[41] and Samelson and Lempicki.[42] The results all strongly indicated that chelates possessed the necessary decay times, line widths, and quantum efficiencies to make them prime candidates for liquid lasers especially. More quantitative evaluations of the laser possibilities, backed up by quantum yield measurements, were reported by Winston *et al.*,[43] who described the fluorescence of europium thenoyltrifluoroacetonate and evaluated the laser threshold parameters.† From their measurements a required laser threshold concentration of excited europium thenoyltrifluoroacetonate molecules in acetone at room temperature was calculated to be 2.3×10^{17}/cc for a cavity with an optical loss of 1%/cm. This evaluation rested upon an absolute quantum efficiency measurement for the molecule of 56% reported by Gudmundsen *et al.*[44] for the fluorescence at 25° C.

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† Although it is convenient to review the papers on laser developments by referring to the compounds by the names used in the publications, the reader is warned that considerable confusion existed for a while over the exact chemical nature of the compounds studied. An account of this confusion is contained in Section V-A of this review and Ref. 28.

Optical maser action of a chelate was first claimed by Wolff and Pressley[45] for europium tris[4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione] in polymethylmethacrylate. By pumping in the organic absorption band of the molecule at about 3400 Å, an efficient energy transfer to the $^5D_0$ level of the Eu^{3+} ion was obtained and the laser transition occurred at 6130 Å between the $^5D_0$ and $^7F_2$ levels, the latter lying about 1000 cm^{-1} above the ground state. Long polymethylmethacrylate filaments containing 10^{-4} mole fraction of the chelate were employed and fluorescence lifetime shortening due to stimulated emission was reported. The experiments were carried out at liquid-nitrogen temperature using a standard Xenon flash lamp as a source. This report has been questioned.[46]

Authentic optical maser action in solution was first reported by Lempicki and Samelson[47] employing a rare-earth chelate as the active material. These investigators used a 3:1 mixture of ethyl and methyl alcohols as a solvent and obtained laser action from concentrations of 5.2×10^{18} molecules/cc in solutions cooled to between $-120°$ and $-170°$C where they become highly viscous liquids. Laser action was observed at 6131 Å. Relaxation phenomena were reported and the characteristic laser spiking as well as line narrowing was seen. This report left no doubt that laser action of the europium benzoylacetonate in a highly viscous medium had been demonstrated. The authors followed quickly with a report of abortive attempts to lase europium dibenzoylmethide in the same solvent system under identical conditions.[48] Although the dibenzoylmethide molecule demonstrated a high yield of fluorescence and a similar pattern to that of the benzoylacetonate, it, unlike the benzoylacetonate, showed neither a definite threshold nor relaxation oscillations. An irregular fluorescence output was observed only with optical feedback present and the authors concluded that a quenching mechanism was operating, preventing laser action.

An independent report of stimulated emission of rare-earth chelates, the benzoylacetonate chelate of europium, was made by Schimitschek[49] who employed a capillary quartz tube and a different cavity geometry than that of Samelson and Lempicki. Again laser action was observed at 6130 Å. Spiking, now characteristic of such phenomena, was seen and line narrowing was observed. In addition, mode patterns were photographed and studied as a function of pump power above threshold.

Probable stimulated emission of terbium tris[4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione] was reported by Huffman who observed irregular wiggles in the fluorescence output of the terbium ion when the pump power exceeded a certain value.[50] This was interpreted as stimulated optical emission of the terbium ion chelate in the vinylic resin. No spiking or line narrowing was observed, however. His conclusions were questioned by Brecher *et al.*[51] who reported similar wiggles of fluorescence outputs for europium chelates of thenoyltrifluoroacetone, benzoylacetone, and dibenzoylmethane and the benzoylacetonate complex of terbium. They were able to show that unusual traces of the fluorescence output *vs* lifetime can be obtained for europium benzoylacetonate complexes, if one just changes the solvent from an alcohol mixture to a mixture of ether, 3-methyl pentane, and alcohol. In the former case laser spiking and definite laser relaxation phenomena are observed; in the latter solution unusual intensity variations of fluorescence output with time are seen when optical feedback is present, but no real laser action occurs. Further experiments by Kudryashov *et al.*[52] on europium dibenzoylmethide under pulse excitation led to the conclusion that stimulated emission was not being observed and that the unusual fluorescence output curve could even be obtained without mirrors on the cell. It is apparent that some unusual phenomena are occurring with these highly luminescent materials during high levels of excitation, but the complete explanation of the curves is not yet clear.

Laser emission at 6130 Å from a cooled alcohol solution of europium benzoylacetonate was verified by Bhaumik *et al.*[53] who emphasized the importance of the preparation and characterization of the compounds. These authors clearly demonstrated that the laser phenomena observed by Samelson and Lempicki[47] were not arising from a trisbenzoylacetonate of europium but were actually arising from a compound having four benzoylacetonate ligands and a piperidinium ion in it. Additional evidence of laser action in europium benzoylacetonate was provided by Bazhulin *et al.*[54] who also reported experiments on the terbium benzoylacetonate complex, although no laser action for this compound was indicated. Stimulated emission in a modified europium dibenzoylmethide, that is, modified by the addition of dimethylformamide to the alcohol solution, was reported by Schimitschek and Nehrich.[55] Above a threshold pump energy the characteristic line narrowing, spiking, and beam collimation were observed. The laser transition lay at 6120 Å and narrowed from 6 to less than 1 Å during laser action. The importance of the dimethylformamide in the solvent was verified by the fact that no laser action occurred when only dibenzoylmethide or the piperidinium adduct of the four ligand complex was used. The dimethylformamide is a necessary ingredient for laser action. These authors also reported experiments on the trisdibenzoylmethides and trisbenzoylacetonate dihydrates of europium, but they were not successful in obtaining laser action from the materials. They conjectured that a reasonable way to account for the difference in the optical behavior of the compounds is to assume a coordination number of 8 or 9 for the europium in the lasing molecules.

Another interesting chemical modification yielding a new laser material was made by Nehrich *et al.*[56] who substituted ammonia for piperidine in the synthesis of the complex and obtained laser action from the tetrakisbenzoylacetonate of europium. They also obtained laser action from the analogous compound containing trifluoroacetylacetonate as a ligand. Curiously this latter molecule lases in the $^5D_0 \rightarrow {}^7F_2$ group when prepared with ammonia but does not lase whenever it is prepared with piperidine. The benzoylacetonate, however, lases when it is prepared with ammonia or with piperidine as a precipitating agent. These authors established that piperidine, the hitherto exclusively used precipitating base, could be successfully replaced in certain compounds by ammonia and probably by several other bases. They also demonstrated that in the trifluoroacetylacetonate complex the substitution is necessary to achieve laser action and hence concluded that the base strongly influences the fluorescence spectrum and the effectiveness of intramolecular energy transfer.

The effect of the action in the complex on the laser action was demonstrated by Meyer *et al.*[57] They prepared a sodium salt which they formulated as the sodium tetrakisbenzoylacetonate of europium and which was very insoluble except by addition of dimethylformamide to the solvent. When exposed to ultraviolet excitation it was found to lase at 6111 Å. This is a considerable shift from the 6130 Å laser line observed for the usual benzoylacetonate complexes and shows the effect of the cation and possibly the dimethylformamide on the laser frequency.

An ingenious method for changing the laser frequency was demonstrated by Samelson *et al.*[58] They were able to shift the laser emission of europium benzoylacetonate in solution by addition of inorganic ions. In particular, the laser frequency at 6131 Å obtained from the piperidinium complex could be changed to 6114 Å by addition of successive aliquots of sodium acetate to the original solution. At the extremes of the concentration range laser action occurred only in the principal line of the dominant species, either the piperidinium or the sodium salt. Laser action was obtained simultaneously in both the line at 6131 Å and the new line at 6114 Å by judicious modification of the amount of sodium acetate added. This salt effect enabled for the first time the tuning of a laser by chemical means.

The requirement of low temperatures, approximately −100° C or lower, for laser action was relaxed by switching away from the usual alcohol mixture to acetonitrile as a solvent. Schimitschek *et al.*[59] showed that the tetrakis forms of sodium thenoyltrifluoroacetonate, europium trifluoroacetonate, and europium benzoyltrifluoroacetonate showed laser action in acetonitrile between −20° and −30° C. This was quickly followed by a report by Samelson *et al.*[60] who were able to obtain laser action at room temperature from the tetrakis form of europium benzoyltrifluoroacetonate. This was followed by a report by Schimitschek *et al.*[61] of the room temperature laser action of the tetrakis benzoyltrifluoroacetonate of europium having protonated pyrrolidine as a cation in acetonitrile for a solvent. Thus the goal of a room temperature liquid laser, potentially one that can be circulated and replenished, had been achieved.

Studies of light scattering in a solution of europium benzoylacetonate during optical pumping have been made by Riedel[62] and a detailed description of the characteristics of the europium benzoylacetonate laser is contained in a paper by Lempicki *et al.*[63] who have also recently reviewed the development of chelate lasers.[46]

V. Search for New Luminescent Materials

A. ADVANCES IN THE STUDIES OF CHELATES

The promise of rare-earth chelates as optical maser materials and the successful operation of chelate lasers using the europium ion triggered an intensive investigation of the chemistry of rare-earth complexes and a search for new luminescent materials. The initial search for materials was hampered somewhat by the lack of detailed knowledge of the actual emitting species in the laser, and the literature reflects a steady but increasing appreciation of the chemical problems involved and a more sophisticated understanding of the structures and properties of the complexes which are highly fluorescent.

An early Russian paper on the subject, by Sevchenko *et al.*,[64] reviews briefly the work which was done with emphasis upon the Soviet literature. They report measurements of absorption and luminescence spectra, investigations of the quantum efficiencies and their temperature dependencies, and offer suggestions for methods of luminescence analyses for some of the elements. In this paper the phenomenon of intramolecular energy transfer is reviewed, and measurements on many rare-earth compounds are discussed. The chelating agents are β-diketones, different derivatives of salicylaldehyde and salicylic acid, some derivatives of 8-hydroxyquinoline, α-substituted compounds of pyridine, and many others. They reported that in most cases the composition of the complex was characterized by a metal: addend ratio of 1:3 indicating an octahedral structure for the rare-earth ion, i.e., tris complexes. Since no preparative procedures are given in this paper, it is interesting to speculate about just what species were studied. In all probability, some tetrakis species were present since they are the ones that form most easily for some of the ligands used. The authors mention that measurements of the quantum luminescence efficiencies of solutions of some terbium compounds at −195° C yielded values close to 100% (see references within) which is also indicative of the existence of tetrakis compounds (see below).

The extreme care required to obtain unique and well-characterized chemical compounds of rare-earth chelates was appreciated by Bhaumik and Tannenbaum who describe the effects of impurities on the luminescence of rare-earth chelates.[65] They found that the method of preparation and subsequent purification steps were very important in order for consistent results to be obtained for quantum yields, lifetimes, and spectra. They report for europium benzoylacetonate and europium dibenzoylmethide a dramatic change in the spectrum itself upon purification.† Spectral lines disappeared between steps and often more than one transition was observed in regions of the spectrum where only one is expected theoretically, indicating the presence of more than one species in the impure chelates. At this time it was not yet realized that the impure tris chelates which they studied probably contained large admixtures of the tetrakis form, for it turns out that the pure tris forms are indeed difficult to obtain unadulterated with the tetrakis species.

That the tetrakis form of the europium complexes could be involved was first realized by Metlay[66] who reported lifetime studies for europium trisdibenzoylmethide in both the microcrystalline state and in EPA,‡ and also for the tetrakis form in the same two physical states. The tris complex had a shorter lifetime than the tetrakis one at the same temperature. Furthermore the tris form showed a large temperature dependence while the

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† See footnote on p. 120 concerning nomenclature.

‡ A solution of 5 parts ether, 5 parts isopentane (sometimes 3-methyl pentane), 2 parts ethanol by volume.

tetrakis species showed no temperature dependence from 77° to 300°K within experimental error. He formulated the tetrakis complex as EuD_4 (D = dibenzoylmethide ion)† although its exact nature was as yet uncertain.

A further development in the knowledge of the luminescing species was reported by Ohlman and Charles[67] who found that stable and well-defined solid complexes are formed between EuD_3 and a variety of oxygen- and nitrogen-containing Lewis bases. From their method of preparation of EuD_3 and their subsequent method of adding the Lewis base, there is no doubt that these authors had the correct formula for the compounds in question. They suggested that the method of preparation of EuD_3 used by most authors probably yielded not EuD_3 but a molecule containing excess piperidine as well as excess dibenzoylmethane. This turns out to be the case.

Ohlman and Charles also found that both the lifetimes and relative fluorescences of chelates at room temperature are markedly dependent upon the nature of the Lewis base present. This conclusion was corroborated by Kleinerman *et al.*[23] who found that the use of Lewis bases would increase the fluorescence yield substantially. They observed fluorescent enhancement in liquid, plastic, and glassy solutions of trivalent terbium, europium, and samarium β-diketonate chelates. Many different Lewis bases were used. Although preparative methods are not given, it is probable that the compounds had the compositions ascribed to them.

The exact chemical nature of the europium benzoylacetonate complex which leads to laser emission was established by Bhaumik *et al.*[53] They found the chemical constitution of the microcrystalline solute to be 1 mole of europium with 3 moles of benzoylacetonate, 1 mole of benzoylacetone, and 1 mole of piperidine.

It was shown by Lee and Nugent[68] that a new class of crystalline

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† Each symbol will be identified when it first appears in the article. For the convenience of the reader, however, the definitions are summarized in the Appendix. Although a systematic nomenclature would be preferable, the proper names have rarely been used in the literature, and I have continued the malpractice here.

rare-earth chelate compounds could be prepared, each member having the empirical formula EuB_4HX (B = benzoylacetonate ion; X = Lewis base). Three of these compounds were studied thoroughly by Nugent *et al.*[69] in microcrystalline form under high resolution. They were EuB_4HP, EuB_4HM, and EuB_4HE (P = piperidine; M = morpholine; E = diethylamine). Of some physical and chemical consequence is the fact that the authors reported that the same emission could be obtained from alcohol solutions of all three compounds, and it thus appeared that the emitting chelate species in alcohol solution was the same in all cases. They postulated an ionization of the chelate in alcohol solution to produce an EuB_4^- ion and a species HP^+, HM^+, or HE^+. This appears to be the first well-substantiated evidence that the emitting species for the laser is the tetrakis anion. Identical conclusions were reached by Brecher *et al.*[70] who found definite evidence for eightfold coordination in europium chelates and reported that the method of preparation with piperidine for both the benzoylacetonate and dibenzoylmethide chelates led to a piperidinium salt of the 4-ligand chelate. These authors were able to analyze the spectra on the basis of a dodecahedral arrangement of the ligands about the europium ion (see Section VI-A,B).

A definitive paper, both from a structural and a chemical point of view, was published by Brecher *et al.*[27] They investigated the emission spectra of both the tris and the tetrakis forms of four β-diketonate chelates of europium in the solid, in the powder, and in alcohol solutions with and without dimethylformamide added. They observed partial dissociation of the tetrakis form in solution and obtained a quantitative measurement of its degree. The β-diketones chosen were acetylacetone, benzoylacetone, benzoyltrifluoroacetone, and dibenzoylmethane. The studies show clearly that the tetrakis forms of all but the benzoyltrifluoroacetonate chelate largely retain their tetrakis composition in alcohol, although some dissociation occurs, whereas the benzoyltrifluoroacetonate chelate completely dissociates. By a simple spectroscopic method based on the emission properties of the chelates they were able to determine the percent of dissociation in alcohol solution of the tetrakis chelates and, surprisingly enough, the least dissociation encountered in alcohol solution is 24% for the EuA_4HP product ($A =$ acetylacetonate ion). The role of dissociation in preventing or, in some cases, allowing laser action to occur and the key role played by dimethylformamide in making the dibenzoylmethide laser possible are elucidated in this study. These authors also reported information on the tris complexes of the chelates and they concluded that the tris chelates, although interesting from a chemical point of view, are not nearly as well suited for laser applications as the tetrakis compounds. The former have not yet shown any kind of laser action. The structural implications in this paper will be discussed in Section VI-A,B.

The dissociation of chelates in solution was also verified in very neat experiments reported by Bhaumik.[71] He showed that the fluorescence of europium hexafluoroacetylacetonate, which occurs at 615 mμ in alcohol solution, can be quenched by adding terbium nitrate to the chelate solution, wherein the strong europium red lines are readily replaced by terbium green lines. The europium fluorescence from the chelate reduces to half intensity upon addition of an equal concentration of terbium ion to the solution. At a terbium concentration of nearly 10^3 times that of europium the red fluorescence is completely replaced by the green one. These experiments, and others reported in the note, clearly demonstrate that a rapid exchange is occurring in the chelate solutions and indicate possible means by which the exchange can be studied by spectroscopic methods. The disappearance of red europium lines and the appearance of green terbium ones is a spectacular demonstration of the exchange process.

A clear picture of the confusion which existed about the exact chemical nature of the chelates synthesized and a reliable resolution of the problem is presented in a paper by Bauer *et al.*[28] A brief history is given of the methods used for the preparations of chelates and the case for the formation of tetrakis complexes is clearly presented. They report two series of compounds with compositions, $C^+[(\beta\text{-diketono})_4Ln(III)]^-$ and $C^+[(\beta\text{-diketono})_3BLn(III)]^-$, in which C^+ is a substituted ammonium cation, B (in this case) is a neutral bidentate ligand, and Ln is europium, gadolinium, or terbium. They present detailed methods of preparation, physical properties including fluorescence spectra, and the chemical and spectroscopic evidence for eight equivalent oxygens in a tetrakis β-diketonate chelate. Strong arguments for octacoordination are presented. These authors are aware of the dangers of dissociation in solution and present the chelates as being subject to dissociative reactions in which the lanthanide ion assumes a variety of coordinations with the ligands and with the solvent molecules.

B. SYSTEMATIC SYNTHESES

An attempt to broaden some of the areas of rare-earth coordination chemistry, to prepare a variety of new crystalline complexes, and to systematize a number of preparations was made by Melby *et al.*[72] These authors prepared a series of complexes of the rare earths, some with neutral donors such as 4-picoline-N-oxide, triphenylphosphine oxide, 1,10-phenanthroline, and tripyridyl. They also prepared β-diketonates complexed with additional nitrogen and oxygen donors and obtained highly fluorescent materials which contained three-bidentate oxygen ligands and one neutral bidentate nitrogen-donor ligand, such as 1,10-phenanthroline or dipyridyl, around the central ion. They remarked that in the solid state or in solution the fluorescence of these compounds is brighter than that of the parent hydrates. They also made analogs of these compounds having aromatic or fluorine substitutents in the β-diketone moieties and obtained a marked increase in fluorescence intensity. Using oxide donors several highly fluorescent europium compounds were obtained of the general formula, tris β-diketonate di-(N-,P-oxide)donor. The anionic tetrakis β-diketonates were also prepared and the previous conclusions concerning the octacoordination of these anions were corroborated. Complexes with a variety of cations were prepared and showed varying degrees of fluorescence. Some cations were shown to effectively quench fluorescence. The authors went on to discuss the emission spectra of Eu^{3+} complexes, ascribing them principally to the $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, and $^5D_0 \rightarrow {}^7F_2$ transitions of the Eu^{3+} ion, and gave evidence for dissociation in alcohol solution and the temperature dependence of it. Their paper contains detailed methods for preparing the complexes and emission spectra of solids and solutions to back up the chemical conclusions.

Similar but less extensive studies were carried out by Butter and Kreher[73] who showed that the fluorescence of various europium chelates, such as the dibenzoylmethide, benzoylactonate, acetylacetonate, and β-naphthoylacetonate, is greatly enhanced by additional coordination of *o*-phenanthroline or α-α'-dipyridyl. They prepared complexes of compositions, europium(β-diketone)$_3$-phenanthroline, europium(β-diketone)$_3$dipyridyl, etc. that could be isolated, and the absorption and fluorescence were studied in various solvents. These authors noted that, compared to the tris chelates, the temperature dependences of the mixed-ligand chelates were remarkably reduced. Preparative methods are given. A thorough reading of references 28, 72, and 73 provides one with an accurate and detailed account of the present status of the coordination chemistry of europium complexes.

Although for most of the highly fluorescent compounds the $^5D_0 \rightarrow {}^7F_2$ transition is undoubtedly the strongest, an anomalous case appears now and then. For instance, in the spectra of the *o*-phenanthroline and α,α'-dipyridyl adducts of europium tris-dibenzoylmethide not only is the fluorescence intensity for the species having adducts strongly increased over the intensity observed for the corresponding tris complexes, but the emission from the $^5D_1$ level of the europium ion is more intense than normally observed for other chelates (line groups at 5350 and 5600 Å).[73] Anomalous results were reported by Lorier and Heindl[74] who prepared the tris-5-nitro-1-naphthalene-1-sulphonate of europium and found the most intense transition to be centered about 5930 Å rather than the usual 6130 Å. They attributed this transition to $^5D_0 \rightarrow {}^7F_1$ (in contrast to the $^5D_0 \rightarrow {}^7F_2$ usually found) and thus this compound distinguished itself by obeying selection rules which allow a different transition to account for most of the intensity.

A systematic study of the effects of substituents upon intramolecular energy transfer was carried out by Sager *et al.*[12] who worked with rare-earth β-diketonate chelates. They prepared two series of complexes. Substituents with different electronegativities were attached in various positions either on a dibenzoylmethide structure (Series A) or directly to the β-diketone ring (Series B). These included symmetrically and asymmetrically substituted β-diketonates having aromatic and/or aliphatic substituents appended to the chelate ring. Absorption spectra in the near ultraviolet region characteristic of π—π^* electronic transitions of the chelates are discussed and phosphorescences at liquid-nitrogen temperature in EPA of gadolinium β-diketonates are presented and described. Detailed syntheses are not given but preparative methods indicate that they probably had mostly tris with some admixture of tetrakis chelates. In a second paper by these authors[13] substituent effects on intramolecular energy transfer are discussed and spectroscopic results of europium and terbium β-diketonate chelates prepared by the method described earlier[12] are presented. One can only assume that the results probably apply mostly to tris complexes.

Rather unusual complexes of europium prepared in a search for luminescent materials are reported by Charles[75] who synthesized mixed-ligand complexes derived from dibenzoylmethide and carboxylate anions of the general formula $(C_{15}H_{11}O_2)_2EuOCOR$. The distinguishing feature of this paper is that the author used thermogravimetry, differential thermal analysis, and thermomanometric analysis, in addition to chemical analysis, to characterize the compounds. Detailed analytical procedures for the rare-earth salicylaldehyde chelates of various rare earths, backed up by thermogravimetric analysis, were reported by Charles,[76] and a fast accurate preparation of europium thenoyltrifluoroacetonate was published by Charles and Ohlman.[77] The emphasis here is on the chemistry and there is little doubt that the empirical formulae are accurately known.

An interesting physical study is reported by Bhaumik[78] who was able to measure the vapor pressure of europium hexafluoroacetonate at 90° C and obtain a value of about 7 microns. Although most rare-earth chelates decompose upon melting and are difficult to hold in the vapor phase, Bhaumik was able to accomplish this with the fluorinated β-diketonate chelate. The pressure measurement offers an interesting application of absorption spectrophotometry, for it was assumed that the π—π^* electronic transition of the chelate would have the same extinction coefficient in the vapor phase as it has in the solid phase or in solution and that, therefore, the optical pathlength could be accurately measured spectrophotometrically and hence the pressure calculated. One fly in the ointment was that the fluorescence of the sublimed product was not the same as the initial substance indicating that some decomposition occurred during the sublimation.

The preparation and luminescence of trishexafluoroacetylacetonate of europium were also reported by Halverson *et al.*[18] and data in various solutions are presented. The presence of moisture had a marked effect on the spectral appearance of the luminescence near 6100 Å signalling chemical complications. These authors have launched a program to systematically design complexes having low radiationless energy losses and high fluorescence quantum yields, employing ligands that shield the complexes from radiationless energy degradation.[79] "Synergic agents" that further protect the molecules in solution and the solid are also used. Synergic agents are such neutral molecules as trioctalphosphine oxide, tributylphosphate, and dihexalsulfoxide which complex the chelate and protect it from external perturbations. Preparative procedures and analytical data on a variety of such highly luminescent compounds are reported.

Additional synthetic methods and a list of compounds having synergic agents with extended chromophors are reported by the same authors in a third paper of the series.[80] The analytical techniques and the preparative procedures indicate that the compounds do have the empirical formulas quoted. These authors also discuss the equilibrium in solution and the possible dissociation of the synergic-agent complex back to a tris complex. They report that considerable dissociation occurs for certain of the molecules. An interesting and important aspect of the compounds synthesized is that the synergic-agent complexes are readily soluble in methylcyclohexane, a non-coordinating solvent. Some compounds with a room temperature quantum efficiency of 80% were made.

An interesting series of complexes of rare earths with 2,2′-dipyridyl of the type $[M(dip)_2(H_2O)_n]^{+3}X_3$, where M^{+3} = rare-earth ion, dip = dipyridyl, $X = Cl^-$ or NO_3^-, and n = number of water molecules, was described by Sinha[81] who gives methods of preparation and isolation. Attempts to prepare a europium complex with three moles of dipyridyl failed. The chemistry of the complexes is discussed in the paper and preliminary observations of the fluorescence properties are reported. Analyses of the infrared data are also presented. A second paper[82] discusses reflection spectra; and a third, substitution effects.[83]

Spectroscopic studies of these dipyridyl compounds were reported by Sinha, Jørgensen, and Pappalardo,[84] and, in addition, the europium phthalate and naphthalate were also prepared and discussed in the latter publication. Fluorescence of terbium phthalate is reported by Sinha,[85] but he obtained no terbium fluorescence from the naphthalate compound.

Rare-earth monoterpyridyls of the type $M(terp)Cl_3 \cdot nH_2O$ where terp = terpyridyl and $n = 1$ to 2.5 have been prepared by Sinha[86] and their ultraviolet, visible, and infrared spectra have been investigated. Preparatory techniques are included in the article and analytical data for the compounds are listed. One unusual result is that the Eu^{3+} ion is the only ion that forms a bisterpyridyl complex; all the others apparently form only the monoterpyridyl compound. Preliminary observations of the luminescence of the Eu^{3+} terpyridyl and the Tb^{3+} terpyridyl complexes are reported by Sinha in a second paper of this series.[87] He states that all emission arises from the $^5D_0 \rightarrow {}^7F$ transition group of europium and the $^5D_4 \rightarrow {}^7F$ of terbium. Photoluminescence of Sm^{3+}, Dy^{3+} and Tm^{3+} terpyridyl chelates are reported in a third publication.[88]

Two papers reflecting the search for luminescent materials in rather unusual areas are by Pappalardo and Losi[89] and Gurevich and Solov'ev.[90] The former authors have obtained *band* emission from gadolinium and lanthanum tricyclopentadienide but report that in other rare-earth cyclopentadienides the energy decays via radiationless transitions involving ^4F_n levels. No intra-4f transitions were reported. The Russian authors discuss the luminescence of rare-earth phthalocyanines and give a preparation for the trivalent phthalocyanine compounds where the third valence is saturated by chloride or hydroxyl. Again no intra-4f transitions were observed.

VI. Structural Investigations

The intense fluorescence observed from europium compounds, including inorganic salts, makes the ions quite amenable to group theoretic analyses of the spectra to determine the symmetry at the europium site. It was recognized years ago by Joos and Hellwege[91] that the upper levels were the $^5D_0$ and $^5D_1$ and later work by Sayre, Miller, and Freed[92] on fluorescence and absorption spectra of Eu^{3+} in alcohol solutions revealed the splitting of the $^7F_1$ and $^7F_2$ states into three and five levels respectively. In chelates an analysis of the europium spectrum should also lead to some knowledge of the site on which the europium ion is situated and therefore *ipso facto* to information concerning the bonding. The analysis is facilitated in chelates because the luminescence is intense and occurs in a region of the spectrum which is easily photographed, or recorded photoelectrically, on high resolution spectrographs. Spectra of both solutions and solids can be analyzed.

A. Spectroscopic Studies of Solids

The first published attempt to analyze the spectrum to determine a site symmetry for the europium ion in a solid chelate was made by Bhaumik[93] who correlated the $^5D_0 \rightarrow {}^7F_2$ transition of the europium ion, the intense transition, to a D_3 symmetry around the ion. At that time the author thought his substance was europium trisbenzoylacetonate microcrystals whereas subsequent work has shown that he undoubtedly had the tetrakis coordinated compound. That a consistent analysis in terms of D_3 symmetry could be made shows the pitfalls that can trap one on an analysis of an insufficient number of lines in the spectrum. This remark should be kept in mind by the reader when the rest of the data in this section are presented and the conclusions reviewed.

Studies on a europium chelate in the solid state were reported by Samelson *et al.*[94] wherein they analyze the spectrum of europium benzoylacetonate and suggest that the complex is not the tris-benzoylacetonate but a tris complex weakly bonded with a mole of benzoylacetone. From the method of preparation and the authors own subsequent admission the complex was undoubtedly the tetrakis piperidinium compound of europium benzoylacetonate. These investigators recorded many lines in the emission spectrum of the complex at 77° K and analyzed the $^5D_0 \rightarrow {}^7F_0$, $^5D_1 \rightarrow {}^7F_1$, and $^5D_{0,1} \rightarrow {}^7F_2$ transitions. They concluded that the symmetry at the europium ion was tetragonal or lower. It is noteworthy that they were able to classify the transitions from the $^5D_1$ into an A and a B series whose origins are separated by 26 cm^{-1}. That only two series were recorded and not three may just possibly be traced back to insufficient resolution of the instrument. The difficulties in working with microcrystalline spectra are emphasized by the authors who maintain that "since in the solid at 77° K a great many lines appear in emission, it is no longer possible to identify the 0–0 transition with certainty". The identification was made, however, based on several lines of argument and the $^5D_0 \rightarrow {}^7F_0$ transition was placed at 5796 Å, just 4 Å from the position assigned in an independent study.[69] A later publication by Brecher *et al.*[27] presented arguments for the site symmetry of the europium ion in the tetrakis EuB_4HP, EuD_4HP, and $Eu(BTA)_4HP$ (BTA = benzoyltrifluoroacetonate ion) microcrystalline solids. These authors based their deduction for the site symmetry of the ion squarely on the $^5D_0 \rightarrow {}^7F_2$ transition which is the most intense line in the spectrum. In each compound quoted two strong lines were observed, 6132 and 6126 Å; 6120 and 6136 Å; 6114 and 6127 Å respectively. Since selection rules for electric dipole transitions in C_{4v} symmetry allow one non-degenerate and one doubly-degenerate transition and since, for each substance, one line is broader than the other, they deduced a probable symmetry of C_{4v} for the europic ion in all three compounds. This is, incidentally, the same symmetry deduced by them for the dimethylformamide adducts of the compounds in alcohol solution.

Many more tetrakis chelates were analyzed by Bauer *et al.*[28] and once again the analysis of the spectrum for the site symmetry is based upon the strong $^5D_0 \rightarrow {}^7F_2$ transition. Considering the selection rules for this transition and counting the number of lines theoretically allowed for various symmetries, they concluded that, whenever a chelate shows two strong bands for $^5D_0 \rightarrow {}^7F_2$, it would probably be of symmetry D_{2d}, C_4, or C_{4v}, whereas when three bands appear it could have either S_4 or D_2 symmetry; four bands would indicate C_{2v}; five bands, C_2 or lower. Most of the complexes they studied indicated either D_2 or S_4 as the probable site symmetry of the europium ion.

Of all the tetrakis salts investigated, only one, the azabicyclononane salt of europium trisdibenzoylmethide showed five distinct lines for the $^5D_0 \rightarrow {}^7F_2$ transition and the authors concluded a symmetry of C_2.

An exceedingly important fact found by these workers is that the EuD_4HP complex exists in an α and β crystalline form. The α form has a $^5D_0 \rightarrow {}^7F_2$ transition split into three strong lines, one at 6135 Å and a doublet at 6125, 6120 Å. For the same transition in the β form, only two lines are observed, one at 6135 Å and a second one at 6115 Å. The authors tentatively interpret this as a change in symmetry from S_4 to D_{2d} for the α and β forms respectively. Either form could be obtained depending upon the synthetic method used. These authors also found a similar α and β form for EuB_4HP. The $^5D_0 \rightarrow {}^7F_2$ crystal-field components for the α form fall at 6123 and 6130 Å, whereas the β form has the same transition located at 6113 and 6135 Å. Although the number of lines is the same in both cases the splitting is substantially different pointing to a change in the symmetry. Since the same number of lines is observed, the authors indicate that a plausible explanation is D_{2d} isomerizing to C_4 or C_{4v} for α and β forms respectively. The two lines for the α form at 6123 and 6130 Å compare favorably with those observed by Brecher *et al.*[27] for the same compound (6126 and 6132 Å). They, however, assigned the symmetry to C_{4v}

whereas Bauer *et al.*[28] assign it to D_{2d}. The existence of an α and β form is a red light for any further structural investigations on the piperidinium europium β-diketonate tetrakis compounds. It is apparent that very careful synthetic and crystallization techniques must be used in order that the same compounds are being studied by different sets of workers in different laboratories.

The ease of conversion from one crystalline form to the other and from one site symmetry of the europium ion to another is emphasized by Bauer *et al.*[28] who mention "that all the general features demonstrated by these tetrakis chelates of europium can reasonably be ascribed to *structures that are very closely akin to one another*".† It appears that slight distortions of the structures give rise to different numbers of spectral lines caused by the change of the site symmetry about the europium ion, again indicating that the spectra and the structures are much more complicated than originally anticipated.

The highest site symmetry to date suspected for a europium ion in a complex is conjectured for the hexafluorophosphate salt of octakis(4-picoline-N-oxide)europium(III) by Rose and Abramson.[95] These authors ascribed probable symmetries of D_{2d} and D_{4d} to the ion and on the basis of the strength of the ${}^5D_0 \rightarrow {}^7F_1$ transition, the evidence supports the D_{4d} arrangement. This compound is noteworthy since the strongest lines are observed at 5920 and 5940 Å. These transitions are associated with the ${}^5D_0 \rightarrow {}^7F_1$ jump in the free ion and are electric-dipole allowed in a D_{4d} symmetry, whereas the ${}^5D_0 \rightarrow {}^7F_2$ transition, which is normally the strongest in Eu^{3+} chelates, is an order of magnitude or more weaker in this compound leading to the conclusion that it is only magnetic-dipole allowed, thus eliminating D_{2d} symmetry in favor of D_{4d}.

The most comprehensive investigation of the structures of any tetrakis complexes in the solid state was published by Nugent *et al.*[69] These authors analyzed the spectrum of microcrystals of EuB_4HP, EuB_4HM, and EuB_4HE at 77°K. They analyzed the largest number of transitions to date. ${}^5D_0 \rightarrow {}^7F_2$, ${}^5D_0 \rightarrow {}^7F_1$, ${}^5D_0 \rightarrow {}^7F_0$, ${}^5D_1 \rightarrow {}^7F_0$ were all observed, and many of the ${}^5D_1 \rightarrow {}^7F_1$

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† Italics by reviewer.

and $^5D_1 \rightarrow {}^7F_2$ lines were seen although some of them had to be calculated from the levels derived from the analysis of the other transitions. From a detailed unraveling of these energy levels, the authors concluded that the europium site symmetry is C_1, C_{1h}, C_2, or C_{2v}. The crux of the argument is the appearance of the $^5D_0 \rightarrow {}^7F_0$ line in the complexes, which "is forbidden as a magnetic dipole transition by the free-ion selection rules $\Delta J \neq 0$ when $J = 0$, so it is unlikely that it would be observed as a magnetic dipole transition for any ligand-field symmetry". Therefore the $^5D_0 \rightarrow {}^7F_0$ transition must be electric dipole. Building upon this supposition the authors observed a splitting of the $^5D_1$ level from the $^5D_1 \rightarrow {}^7F_0$ transition and the splitting, although small, is measurable. The three lines are 5262.6, 5266.6, and 5268.5 Å for EuB_4HP. The splitting of the $^5D_1$ level into three components is the crucial argument eliminating any fourfold axis of symmetry about the europium ion. Since the preparative procedures and the observed strong transitions match well those of Samelson *et al.*,[94] one concludes that both sets of investigators were working on the same compound. That Samelson *et al.* did not observe splitting of the $^5D_1$ into three levels, but only two, can probably be laid to the lower resolution of the apparatus used, since two of the lines observed by Nugent *et al.* lie less than 2 Å apart and could easily be grouped as one transition. This seems especially plausible since the wavelengths reported contain one more significant figure than the previous work.

A curious identity seems to exist between the spectrum of EuB_4HP and EuB_4HM,[69] and the position of the strong lines indicate that the α form (see Ref. 28) of the complex was being studied. The lower site symmetry for the europium ion is based upon the very small splitting of the $^5D_1$ level, which is difficult to deny from a careful scrutiny of the many lines which were measured and the respectable reproduction of band contours obtained for overlapping lines using the derived energy level values.

It is clear from the papers considered here that a great deal of work has yet to be done before the symmetries of the europium ion in the various complexes are known accurately. The most reliable investigation appears to be that of Nugent *et al.*[69] who have measured and fit many more lines in the spectrum and therefore have determined the system sufficiently to lend credence to the symmetry deductions. It is clear that many of the complexes should be studied in detail and preferably at 4° K before definitive symmetries of the ion can be deduced. It is also apparent that before a detailed analysis is undertaken the synthetic techniques and probable existence of isomeric forms must be carefully considered.

The apparently low energy barrier hindering conversion from one symmetry to another leads one to be suspicious of any extraneous lines appearing in the spectrum of a so-called unique species. Although the spectra should be studied at liquid-helium temperature, there is no guarantee that a phase transition could not occur between 4° K and 77° K and thus two different spectra be obtained. The curious vibronic transitions and intensity variations observed[16, 69] should also supply information concerning the vibrational frequencies of the metal–oxygen bond in these compounds. It is clear from analysis of the papers just reviewed that the spectroscopic structural investigations of these compounds have just begun. No X-ray data have yet, to my knowledge, been reported, although they are vitally needed.

B. Spectroscopic Studies in Solution

As mentioned previously the picture in solutions is considerably complicated by dissociation and solvation phenomena, but a fairly detailed analysis of the symmetry of the europium ion in solution has been given.[27] For the tetrakis chelates dodecahedral structures having D_{2d} symmetry for europium in the benzoylacetonate complex in alcohol, D_{2d} oxygen symmetry lowered to S_4 in the dibenzoylmethide complex in the same solvent, and D_{2d} lowered to D_2 in the acetylacetonate in alcohol have been deduced. Thus in these three cases the evidence "clearly indicates that in alcohol solutions of the four ligand forms, the eight oxygens assume a dodecahedral relation about the central europium ion subject only to slight distortion from steric or solvent interactions". These authors also analyze the spectrum of the dimethylformamide adduct of the four ligand forms in alcohol and deduce a C_{4v} symmetry for the ninefold coordinated species. Cogent chemical and bonding arguments are given for the ligand arrangements, and a model for what happens to the four ligand species in a dimethylformamide solution is presented. Because of the natural line breadth of the fluorescence observed from the europium ion in solutions, it is difficult to see how any better knowledge about the symmetries of the species in solution can be achieved. The symmetries already deduced cannot be verified in all detail but represent highly probable structures for the complexes. If the ease of converting from one configuration to another is as great as painted,[28] then it is doubtful that only one species is contained in solution, but the collisional line broadening will prevent any closer analyses from being made.

Structural implications contingent upon line splitting of complexes in EPA glasses were also discussed by Filipescu *et al.*,[13] although the analytical results obtained indicate that not all the compounds were of high purity. This factor makes the reliability of the conclusions difficult to assess.

C. Spectroscopic Studies in Plastics

A preliminary attempt to deduce the structure of a chelate in a plastic medium was published by Voloshin *et al.*[96] who carried out a spectroscopic study of europium benzoylacetonate in a polymethylmethacrylate matrix. Preparative methods are not given in this paper, and it is difficult to ascertain what compounds were actually investigated, but the authors concluded that the complexes have very low symmetry (no higher than rhombic), that the $^5D_0 \rightarrow {}^7F_2$ transitions are the strongest, and, surprisingly, that the symmetry of the crystal field around the europium ion is the same as in the crystalline samples. Some fuzzing out of the lines is observed in the plastic, however, where the line width is two- to threefold greater than in the solids. A number of weak lines, which were not assigned, definitely appeared in the plastic; these are tentatively considered to be vibrational frequencies superimposed upon the electronic transitions. In the light of the subsequent work in solutions this is probably an incorrect conjecture; the more probable one is that several species were actually present in the plastic and that therefore multiple symmetries were available for the europium ion.

A detailed investigation of europium tris[4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione] chelate dissolved in polymethylmethacrylate was carried out by McAvoy *et al.*[14] Multiple, overlapping, broad lines were observed. From the preparative procedure used, it is likely that the tetrakis piperidinium complex was formed but whether it remains intact in the plastic is a moot point. The authors mention, however, that the phosphorescence present for the gadolinium chelate dissolved in the host was completely quenched when europium replaced gadolinium. This leads one to suspect that a large number of tetrakis molecules remained in the plastic although the authors assumed a tris species.

It appears that in plastics, just as in solutions or glasses, any symmetry analysis is going to be exceedingly difficult, and in most cases only vague general conclusions will likely be forthcoming. Crystals hold much greater promise.

VII. Quenching

Certainly the least understood of the processes which occur to yield luminescence from a complex molecule are those which come under the general heading of radiationless transitions. In a rare-earth complex the primary act of absorption usually raises the molecule to an excited vibrational level of the lowest singlet state (S_1) from which there is rapid internal conversion to the lowest vibrational level of the singlet, then (assuming a triplet path for transfer, see Section II-A) intersystem crossing to the triplet manifold of levels occurs followed by further internal conversion to the lowest triplet (T_1) (or one which is only slightly above the lowest one owing to thermal population). This sequence of events is followed by a second radiationless process wherein energy migrates to the rare-earth ion levels (intramolecular energy transfer). The rare-earth ion then relaxes to a condition in which the excitation energy resides in a so-called resonance level. Finally, emission occurs via a radiative combination between the resonance level and a lower level, usually a term derived from the ground-state multiplet.† The detailed mechanism responsible for any one of these radiationless transitions permitting the energy to migrate from one system of levels to another is not understood.

Competing with these radiationless transitions facilitating energy transfer are also radiationless processes which reduce the luminescence yield by degrading the energy to heat. The molecule can be quenched at various stages during the energy migration; quenching from the lowest singlet, quenching from the triplet manifold, and finally, quenching from the rare-earth ion states occur to some degree in all complexes and reduce the yield of emitted light. From the standpoint of designing complexes for optical masers, it is paramount to reduce these degradative processes to a minimum and thus keep the yield high enough for practical applications. From a fundamental point of view, these rare-earth complexes offer systems exceedingly well-suited for the study of quenching in some detail.

Three methods of studying the quenching processes have been used during investigations of rare-earth chelates. The first and most difficult technique employs measurements of the total quantum yield of luminescence for the complexes. Absolute yield measurements,[44] which are rather difficult experimentally, or relative yield measurements[97] have been carried out. Yield experiments provide an overall efficiency rating for the complexes by measuring the number of photons emitted relative to the number of photons absorbed. Yield measurements alone do not, however, supply information concerning *which step* in the energy migration process is subject to quenching. Studies of quantum yield *vs* temperature are highly informative concerning when quenching becomes important. The second and somewhat easier method of studying quenching is to measure the lifetime of the decay of the luminescence emanating from the chelated rare-earth

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† See Refs. 7, 15, 25 for discussions of these processes.

ion.[17, 36, 37, 41, 42, 66, 98, 99] For rare-earth chelates, especially those of europium and terbium, measurement of the decay time is fairly easy to accomplish, because the lifetimes are long compared with the standard types of flash apparatus now available and the emissions are strong. Temperature dependent studies of the mean lives of decay enlighten one regarding the loss of energy from the *emitting state.* Since, for a decay time measurement, it is generally only possible to observe the strong emission lines, and since this strong emission generally arises from a unique resonance level of the rare-earth ion, then the change in lifetime caused by complexing agent, solvent, or temperature is a direct measure of relative quenching of the resonance level under the various perturbations.[67] The third and most fruitful method of studying quenching is to combine lifetime measurements with quantum yield measurements.[38, 100] This allows one to study both the overall efficiency of the luminescent material as well as the quenching which occurs within the rare-earth ion after the energy has reached the 4f electronic levels. In this way it is possible to learn something about the stage in the migration process where degradative coupling becomes important.

From the studies reported in the literature, it is possible to summarize the present knowledge concerning quenching in rare-earth complexes as follows:

(a) Temperature dependence of quenching. As with most purely organic luminescent materials the total quantum yield of luminescence increases as the temperature is lowered, both for materials in the solid phase (crystals or powders) or solutions. In the former case the temperature dependence is usually smaller than for the latter, and the liquids achieve a high luminescence yield usually only when the materials are frozen to a glass at liquid-nitrogen or near liquid-nitrogen temperatures. Exceptions to this rule are materials which have high quantum yields even at room temperature showing that the effects of solvent or crystal environment upon the degradative mechanisms are not very large.[44, 60, 61, 73, 79, 97]

(b) Quenching in tetrakis *vs* tris complexes. In general the tris complexes of the rare earths have lower quantum yields of luminescence than their tetrakis analogs.[27, 65, 66] For a given ligand the lifetime of the decay of the fluorescence from the central chelated rare-earth ion is substantially shorter for tris than for tetrakis forms reflecting the lower quantum yields and stronger quenching of the resonance levels.[99] It appears that the tris complexes are more susceptible to solvent perturbations because they are less rigidly held together and the holes in the structures allow the solvent to get close enough to create radiationless mechanisms to deplete the quantum yields. For tetrakis complexes, however, the fourth bidentate ligand fills up the structures apparently in such a way as to make them both more rigid and less susceptible to the approach of solvent molecules. These factors evidently increase both the *total measured quantum yield* and the quantum yield from a resonance level for a particular complex.

(c) Reducing quenching by "protecting" reagents. Both the tetrakis and tris complexes can have their quantum yields significantly increased, the former somewhat and the latter markedly so, by shielding the rare-earth ions through a judicious selection of reagents which will make the structures even more rigid about the ions and thus protect the excited complex from losing energy to the surroundings.[23, 67] So-called "synergic reagents" are being used to tie up the additional orbitals available for bonding in tris complexes in such a way that the yield and the lifetime both increase significantly.[79, 80] The prerequisites for such reagents to be effective are that (1) they have no low-lying energy levels which can drain off the energy from the complex and thus act as an energy trap and (2) the reagents themselves must be sufficiently rigid and chemically inert to shield the rare-earth ion in the chelate from further influences of the environment.

(d) Reducing quenching by chemical substitution. Significant increases in quantum yields and also lifetimes of decays of complexes can be achieved by making substitutions on the ligand part of the chelate molecules.[12, 13] An example is the substituting of fluorine for hydrogen on a parent complexing ligand such as benzoylacetone or acetylacetone. The general effect of the fluorine substitution is to modify the chemical properties (such as basicity) of a ligand somewhat, but the increases in quantum yield and lifetime of decay which are observed for the complex can be traced back mainly to the protection of the rare-earth ion from the effects of high vibrational frequencies. It appears that the elimination of the high-frequency vibrational modes in the complexing ligand has the effect of reducing the efficiencies of radiationless processes. The bulk of the experimental evidence has been interpreted to mean that the primary mechanism for radiationless degradation of the energy stored on the central-metal ion in a chelate is through a vibronic interaction with the ligand and thence to the solvent.[100] This explanation appears very plausible especially with regard to deuterium substitution wherein a chelate molecule can significantly increase its quantum yield of luminescence as well as the lifetime of the decay of the resonance level of the rare-earth ion merely by having deuterium atoms substituted for hydrogen atoms in the ligand framework. The large increase in mass of deuterium over hydrogen evidently has the effect of enhancing the quantum yield through reducing the number of high-frequency modes around the ion, modes which provide an efficient means of coupling excitation energy to the environment in a radiationless manner. Significant increases in yield can even be obtained by changing the solvent from a usual protonated one to a perdeuterated substance, for instance, by substituting D_2O for H_2O or even CH_3OD for CH_3OH in the solvent used to dissolve the chelate molecules.[101-106] That enhancement of the total quantum yield and increase in the lifetime of luminescence occur from such a modification is certainly direct evidence that the solvent often plays a primary role in the radiationless deactivation mechanisms and that, for some chelate molecules, the solvent is by no means an inert reagent from the standpoint of luminescence processes.

VIII. The Design of Luminescent Materials

The general knowledge now available concerning the intramolecular energy transfer phenomenon, coupled with the experimental means cited above for increasing the quantum yields and lifetimes of decays of the luminescing complexes, can be used for guidance in the design of new luminescent materials having exceedingly high quantum yields (approaching 100%) and long decay times approaching the theoretical *intrinsic* decay times of the excited states of the rare-earth ions. To build such highly desirable luminescent substances one should usually synthesize a tetrakis complex having its triplet state above the resonance level of the rare-earth ion, use a ligand which is perdeuterated (if chemically feasible), protect the molecule thus formed by an additional adduct or synergic reagent which is spectroscopically inert but has good solubility properties, and dissolve the complex in a solvent which is perdeuterated or which at least contains a minimum of hydrogen vibrational modes. Although all these restrictions appear to put undue limitations on the compounds and solvents, it is encouraging that some systems incorporating many of the features listed have already been found and that the future for making luminescent substances having highly interesting and useful properties is bright. One can predict substantial advances in the design of such materials and in the techniques for synthesis and characterization of them. Concommitant progress in both the experimental and the theoretical investigations of the intramolecular energy transfer phenomenon displayed by these molecules can also be expected.

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APPENDIX

Abbreviations used in the review:

Symbol	Ion or Compound
A	Acetylacetonate ion
B	Benzoylacetonate ion
D	Dibenzoylmethide ion
E	Diethylamine
M	Morpholine
P	Piperidine
X	Lewis base
BTA	Benzoyltrifluoroacetonate ion
8HQ	8-Hydroxyquinolate ion