The time integral of the interaction energy regarded as an impulse of duration $\tau$ is estimated to be $V_b\tau$, where $V_b$ is the value of $V(t)$ at the distance of closest approach $b$ between the colliding molecules; $\tau$ is the duration of the collision and is of the order $b/\bar{v}$, where $\bar{v}$ is the average relative velocity. Now the magnitude of the interaction between the electrostatic field of the polar molecule and the dipole moment induced by this field in the foreign molecule may be dimensionally represented by

$$V_t \approx \sum_n \frac{C_n \alpha}{b^n} . \qquad (8)$$

Then, regarding the collision diameter $b_{nr}$ as that distance of closest approach for which $\mid a \mid^2$ reaches some given value (of the order of unity), we have from (7) and (8), provided one of the terms in (8) predominates over the others,

$$b_{nr}^2 \approx (\alpha/\bar{v})^{2/(n-1)}. \qquad (9)$$

In accordance with (9) we have plotted $\log b_{nr}^2$ vs $\log(\alpha/\bar{v})$ in Fig. 3, where it is seen that the data for the nonpolar broadening gases can be reasonably well represented by straight lines. Not included are the data for He and $H_2$, which fall rather far below the lines, the deviation being especially pronounced in the $CHF_3$ mixtures. As might be expected, the nonresonant cross sections for those gases possessing a sizeable dipole or quadrupole moment lie above the lines, indicating that the cross sections for these gases is greater than may be expected on the basis of an interaction involving only the dipole moment induced in the foreign molecule by the polar molecule.

Despite the reasonable correlation of $b_{nr}^2$ with $\alpha/\bar{v}$ (excepting the data of He and $H_2$), (9) in fact fails in the following important way. The dominant interaction between a polar and nonpolar molecule is of the dipole–induced-dipole type $(n=6)$. Then according to (9), the slope of the lines in Fig. 3 should be 0.4, whereas the slope of the line for the $CH_3Cl$ mixtures is, for example, 0.54.

# Photoluminescence of Lanthanide Complexes. II. Enhancement by an Insulating Sheath

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The effect of an "insulating sheath" in reducing radiationless energy losses from a lanthanide chelate is postulated and techniques for developing this sheath are described. Data on luminescence of various europium chelates and synergic agent complexes are presented which demonstrate the efficacy of the sheath. A quantum efficiency approaching 80% is obtained for photoluminescence of a low viscosity hydrocarbon solution at room temperature.

## INTRODUCTION

THERE are many nonradiative mechanisms for the loss of energy from molecular systems in excited electronic states. All of these mechanisms, however, depend on the presence of an energy acceptor, and the rate of transfer depends on the coupling between energy donor and acceptor (as well as on the multiplicity of acceptor states).

If energy acceptors differ only in the number of quanta of excitation required in the final state, it might be expected that Franck–Condon factors[1] would favor (provide the higher rate to) the acceptor requiring the least number of quanta. If the acceptors differ only in proximity to the donor, it might be expected that the coupling would be greater for the closer acceptor (providing the larger rate). In the limit, the stronger the bond (van der Waals or otherwise)

between the acceptor and donor, other factors being equal, the larger the transfer rate expected. Thus in order to minimize radiationless energy transfer, it would appear desirable to enclose the "electronic energy-rich moiety" (potential donor) in a sheath which itself is a poor acceptor and which insulates the donor (maintains a minimum distance) from better energy acceptors in its environment.

We do not explore theoretical aspects[1-3] in the present article, but merely outline a simple experimental approach for developing this "insulating sheath" for lanthanide chelate systems, describe some specific systems, and present preliminary data. Emphasis is on (1) the mismatch of energy levels between donor and sheath and on (2) making the sheath as complete as possible. Results are given for one class of liquid systems. It is in the liquid phase where quenching

[1] G. W. Robinson and R. P. Frosch, J. Chem. Phys. **38**, 1187 (1963).

[2] D. L. Dexter, J. Chem. Phys. **21**, 836 (1953).
[3] M. Gouterman, J. Chem. Phys. **36**, 2846 (1962).

(self, impurity, solvent) of luminescence frequently is a problem.

## INSULATING SHEATH

In the case of $\beta$-diketone chelates of lanthanide (or rare earth) metal ions, $M$ (beta diketone enolate ion)$_3$, the chromophore is directly attached to the central metal ion via the oxygen atoms. Since the chromophore is directly involved in the chelate bond, it is convenient to refer to it as a "chelating chromophore," and in the simplest case has the structure



I.
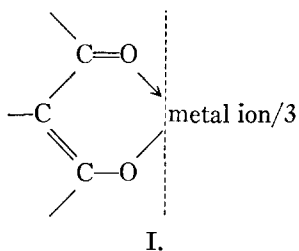
The chromophoric system can be enhanced by attaching unsaturated substituents to the carbon skeleton so as to extend the conjugated grouping. In general the energy levels of the chelating chromophore are the same as those of the $\beta$-diketone enolate ion.

The energy-rich portion of an excited lanthanide chelate consists of the *chelating chromophore* and the *chelated lanthanide ion*, and this is the moiety to be wrapped in the insulating sheath. Since the stored quanta are in the visible or ultraviolet region, the available energy levels in the insulating sheath should be far removed from this range. The sheath should be bulky to prevent the close approach of like systems, quenching impurities, and undesirable solvent components to the energy-rich moiety.

Groupings which satisfy the energy requirements placed on the insulating sheath include saturated hydrocarbons, fluorinated and/or chlorinated hydrocarbons, etc. Of course the exterior of the sheath will determine solvent compatibility, so the solute and solvent system cannot be chosen completely independently of each other.

Two ways in which this bulky insulating sheath can be attached to the chelating chromophore–lanthanide system are (1) by substituents on the chelating chromophore, and (2) by the use of appropriate "synergic agents."

### Substituents

Consider the simplest chelating chromophore
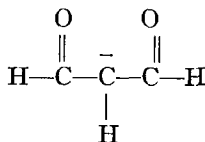


for illustration purposes. (It is unstable chemically, and so no data can be obtained for it.) Substitution of the terminal hydrogen atoms by methyl groups, forming the acetylacetonate ion, represents the start of an insulating sheath. But the methyl groups are not very bulky, and so are not very effective. A considerable increase in bulk can be achieved by the use of tertiary butyl groups, forming the dipivaloylmethide ion. When the tris chelate is formed these tertiary butyl groups appear on the periphery of a rather compact ball-like structure, with the lanthanide ion at the center. From molecular models, however, there still appear to be spaces for penetration by small molecules, and indeed hydrates are observed. Instead of using rigid tertiary butyl groups, long floppy alkyl chains could be substituted.

Even better insulation can be expected from fluorinated hydrocarbon groupings such as trifluoromethyl and pentafluoroethyl. In these cases there may also be more of an effect on the chromophore levels due to the inductive effect of such substituents, than in the case of plain hydrocarbon substituents.

If the chelating chromophore is expanded (by extending the conjugated chain), similar comments apply to all exterior parts of the chromophore.

### Synergic Agents

Since the lanthanide chelates involve tripositive metal ions, and since the $\beta$-diketone enolates are uninegative ions, the neutral chelate involves three negative ligands. When these three ligands are $\beta$-diketones there are six oxygen atoms available for coordination to the rare-earth ion. There is considerable evidence,[4–6] however, that the lanthanide ions prefer seven or eight (or even nine) oxygen atoms in their coordination sphere. (In many cases this desire may be satisfied by water molecules which pass undetected.) This behavior furnishes a means for completing the insulating sheath by using appropriate "synergic agents."[7,8] These are neutral molecules such as trioctylphosphine oxide (abbreviated as TOPO), which have a good lone oxygen atom for coordination to the metal ion, combined with a bulky saturated hydrocarbon tail directed away from the metal ion and hence contributing to the insulating sheath.

In the case of europium ions the stable coordination number for oxygen atoms appears to be about eight. Thus the neutral compounds Eu(chelating ligand)$_3$-

[4] H. Irving and D. N. Edgington, J. Inorg. Nucl. Chem. **21**, 169 (1961).
[5] T. Moeller, *The Chemistry of the Lanthanides* (Reinhold Publishing Corporation, New York, 1963), p. 60.
[6] C. K. Jorgensen, R. Pappalardo, and H. Schmidtke, J. Chem. Phys. **39**, 1422 (1963).
[7] H. Irving and D. N. Edgington, J. Inorg. Nucl. Chem. **15**, 158 (1960).
[8] T. V. Healy and J. R. Ferraro, J. Inorg. Nucl. Chem. **24**, 1449, 1463 (1962).

(synergic agent)$_2$ can be prepared. It is convenient to refer to such molecules as "synergic agent complexes." Typical examples of synergic agent complexes are Eu(TFAC)$_3$(TOPO)$_2$, La(TTA)$_3$(TBP)$_2$, Tb(HFAC)$_3$(TOPO)$_2$, and Eu(HFAC)$_3$(DHSO)$_2$, where TFAC≡trifluoroacetylacetonate, HFAC≡hexafluoroacetylacetonate, TTA≡thenoyltrifluoroacetonate, TBP≡tributylphosphate, and DHSO≡dihexylsulfoxide. Synergic agents of interest in the present context include trialkyl Group V oxides, alkyl dialkyl phosphinates, dialkyl alkyl phosphonates, trialkyl phosphates, and dialkyl sulfoxides.

It is believed that the presence of water molecules coordinated to the metal ion is deleterious,[9] particularly in a hydrogen bonding solvent. The bond is relatively strong, the number of vibrational quanta involved for water to be an acceptor is only five or six, and the hydrogen bonded solvent is a good energy sink. Replacement of the water molecule by the R$_3$P=O molecule (where $R$ is an alkyl group) gives a bond which is not quite as strong, the energy per P–O vibrational quantum is a third as large, and transfer to the remainder of the synergic agent molecule may not be as good as for the hydrogen-bonded solvent. Hence the synergic agent is *particularly useful in the development of an insulating sheath.*

The synergic agent may also contain a chromophore, provided it is protected in the same fashion as the chelating chromophore. Thus the sulfoxide grouping in DHSO provides a chromophore absorbing in the region near 3000 Å. At this point no detailed mechanism is presented for energy transfer from synergic agent chromphore to metal ion, but presumably it will be essentially the same as that involved for the chelating ligand.

## COMPOUND PREPARATION

Compounds and results in the present article are restricted to systems having the simple β-diketone enolate ion chromophore, I. The synthetic details and full discussion of these compounds will be reported elsewhere.

### Lanthanide Chelates

Europium trisacetylacetonate, often abbreviated as Eu(AC)$_3$, and europium trisdipivaloylmethide [Eu(DPM)$_3$] were prepared according to literature procedures[10] by reaction of the sodium salt of the ligand with anhydrous EuCl$_3$ in ethanol. Eu(DPM)$_3$ may also be prepared in acetone from the ammonium salt of dipivaloylmethide and Eu(NO$_3$)$_3$·6H$_2$O. Europium

tristrifluoroacetylacetonate [Eu(TFAC)$_3$] was obtained from the reaction of europium trichloride hexahydrate with a buffered solution of the ammonium salt of the ligand in 50% aqueous ethanol. Europium trishexafluoroacetylacetonate [Eu(HFAC)$_3$] and europium tris - 1,1,1,2,2 - pentafluorohepta - 3,5-dionate [Eu(PFHD)$_3$] were prepared similarly, by shaking a buffered aqueous solution of europium nitrate with a diethylether solution of the ammonium salt of the ligand. The dihydrate of Eu(HFAC)$_3$ is rather easily dehydrated, but the monohydrate of Eu(TFAC)$_3$ cannot be dehydrated without some decomposition.

### Synergic Agent Complexes

The two general techniques used for preparing synergic agent complexes are designated as (A) and (B). In (A) the preformed lanthanide tris chelate is mixed with a dilute hydrocarbon solution of the synergic agent. An excess of the synergic agent must generally be used (mole ratio of synergic agent to europium being in the range 2:1–4:1). Since the chelate usually is insoluble in the hydrocarbon solvent, the reaction may proceed slowly (weeks) at room temperature, but eventually all the chelate disappears. One disadvantage with this method is the difficulty in isolating the complex free from excess synergic agent, but for *qualitative* luminescence studies at room temperature the excess reagent is not harmful. In Technique (B), which is a modification of a procedure[8] used in tracer extraction work, an aqueous solution of Eu$^{3+}$ (as the nitrate) is equilibrated with an ether solution of chelating agent (as the free ligand or as the ammonium salt) plus synergic agent. The mole ratio of chelating agent L to synergic agent S in the ether solution is fixed at 3:2 and the volume of solutions used is adjusted to give a mole ratio of 1:3:2 for Eu$^{3+}$:L:S. The complexes EuL$_3$S$_2$ are formed in almost quantitative yield in a short time, collect in the ether phase, and are isolated therefrom. All of these synergic agent complexes are amber oils which melt near 0°C.

### Analytical Data

The compounds used in the present study are listed in Table I, along with the europium analyses on purified materials. Some of the simple tris chelates can exist as mono- or dihydrates also. While the anhydrous designations are used in the text for convenience, it should be understood that in alcoholic solutions the hydrates and/or alcoholates probably are the main species present.[11]

#### SPECTROSCOPIC DATA

Spectroscopic data in the present article will refer to luminescence of solutions of europium complexes in the

[9] J. L. Kropp and M. W. Windsor, J. Chem. Phys. **39**, 2769 (1963).

[10] *Inorganic Syntheses,* edited by W. C. Fernelius (McGraw-Hill Book Company, Inc., New York, 1946), Vol. II, p. 10; *Inorganic Syntheses,* edited by E. G. Rochow (McGraw-Hill Book Company, Inc., New York, 1960) Vol. VI, p. 147.

[11] F. Halverson, J. S. Brinen, and J. R. Leto, J. Chem. Phys. **40**, 2790 (1964) hereafter designated as Part I.

TABLE I. Analytical data on compounds of special interest.

| Compound | Code[a] | Melting point (°C) | % $Eu_2O_3$ Calc. | % $Eu_2O_3$ Found |
|---|---|---|---|---|
| $Eu(t\text{-}C_4H_9COCHCOC_4H_9\text{-}t)_3$ | $Eu(DPM)_3$ | 157 | 25.08 | 25.00 |
| $Eu(CF_3COCHCOCH_3)_3$ | $Eu(TFAC)_3$ | 275d | 28.80 | 28.90 |
| $Eu(CF_3CF_2COCHCOCH_2CH_3)_3$ | $Eu(PFHD)_3$ | 79 | 21.90 | 21.81 |
| $Eu(CF_3COCHCOCF_3)_3$ | $Eu(HFAC)_3$ | 196 | 22.76 | 22.80 |
| $Eu(t\text{-}C_4H_9COCHCOC_4H_9\text{-}t)_3[(n\text{-}C_8H_{17})_3PO]_2$ | $Eu(DPM)_3(TOPO)_2$ | 5 | 11.93 | 12.01 |
| $Eu(CF_3COCHCOCH_3)_3[(n\text{-}C_8H_{17})_3PO]_2$ | $Eu(TFAC)_3(TOPO)_2$ | 0 | 12.71 | 12.89 |
| $Eu(CF_3COCHCOCH_3)_3[(n\text{-}C_4H_9O)_3PO]_2$ | $Eu(TFAC)_3(TBP)_2$ | 10 | 15.38 | 15.47 |
| $Eu(CF_3COCHCOCH_3)_3[(n\text{-}C_6H_{13})_2SO]_2$ | $Eu(TFAC)_3(DHSO)_2$ | 15 | 16.79 | 16.71 |
| $Eu(CF_3CF_2COCHCOCH_2CH_3)_3[(n\text{-}C_8H_{17})_3PO]_2$ | $Eu(PFHD)(_3TOPO)_2$ | 12 | 11.16 | 12.25 |
| $Eu(CF_3COCHCOCF_3)_3[(n\text{-}C_8H_{17})_3PO]_2$ | $Eu(HFAC)_3(TOPO)_2$[b] | −10 | 11.36 | 11.41 |
| $Eu(CF_3COCHCOCF_3)_3[(n\text{-}C_6H_{13})_2SO]_2$ | $Eu(HFAC)_3(DHSO)_2$ | 0 | 14.54 | 14.42 |

[a] DPM=dipivaloylmethanide; TFAC=1,1,1-trifluoroacetylacetonate; PFHD=1,1,1,2,2,pentafluoroheptanedionate; HFAC=hexafluoroacetylacetonate; TOPO= trioctylphosphine oxide; TBP=tributylphosphate; DHSO=dihexylsulfoxide.

[b] Other microanalyses for this compound (element: calc. %, found %): C, 41.11, 41.30; H, 6.84, 6.99; F, 22.08, 21.94; P, 4.00, 4.12. The accuracy of these results is typical of those for other compounds in the table.

6100–6225-Å region, arising from the $^5D_0 \rightarrow {}^7F_2$ transition of $Eu^{3+}$. Excitation is by absorption in the region 2800–3800 Å. The terminology "alcohol solvent" refers to a 3:1 ethanol–methanol mixture, and "hydrocarbon solvent" refers to a 1:1 methylcyclohexane-3-methylpentane mixture.

## Luminescence Spectrum

The luminescence spectrum was measured using a Perkin–Elmer Model 12C spectrometer modified in four ways. (1) A light flint glass prism replaced the usual NaCl prism. (2) A reflection grating with 1800 grooves/mm replaced the Littrow mirror and was adjusted to augment dispersion by the prism. (3) An RCA 1P21 photomultiplier mounted behind the exit slit was coupled with a Leeds & Northrup high-voltage power supply, amplifier, and Speedomax recorder for detection of radiation. (4) The luminescent solution, excited by filtered radiation from a GE H85A3/U2 mercury arc, replaced the usual Globar light source. In operation the instrument is capable of resolving lines less than 1 Å apart.

A dilute aqueous sodium nitrite filter was positioned at the entrance slit. Calibration was obtained by recording portions of a neon arc discharge spectrum simultaneously with the luminescence spectrum.

Both front surface and side illumination of the luminescent samples were used. For the temperature dependence measurements a cell designed for variable
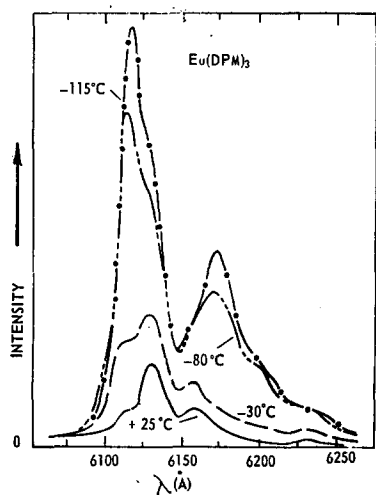


FIG. 1. Luminescence spectrum of alcoholic (3:1 ethanol–methanol mixture) solution of $Eu(DPM)_3$ at several temperatures.
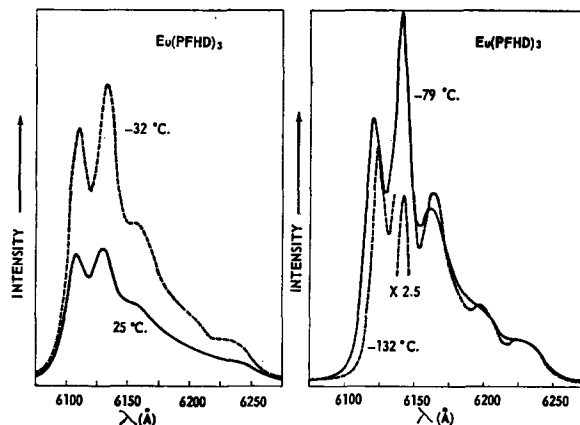


FIG. 2. Luminescence spectrum of alcoholic (3:1 ethanol–methanol mixture) solution of $Eu(PFHD)_3$ at several temperatures.

temperature absorption spectroscopy[12] was used, with front surface illumination. This arrangement permitted good reproducibility of spectral data between the cooling and warming cycles.

The luminescence spectra of alcohol solutions of Eu(DPM)₃ and of Eu(PFHD)₃ at various temperatures are sketched in Figs. 1 and 2, respectively. [Data for Eu(HFAC)₃ were given in Part I, and the luminescence spectrum of Eu(acetylacetonate)₃ at 77°K has been published.[13]] No correction has been made for the change in density on cooling, but otherwise the intensities *for a given solution* are directly comparable at all temperatures. Corresponding data for hydrocarbon solutions of Eu(HFAC)₃(TOPO)₂ and of Eu(HFAC)₃(DHSO)₂ are sketched in Figs. 3 and 4, respectively. While solubilities of the synergic agent complexes in the hydrocarbon solvent are very good at



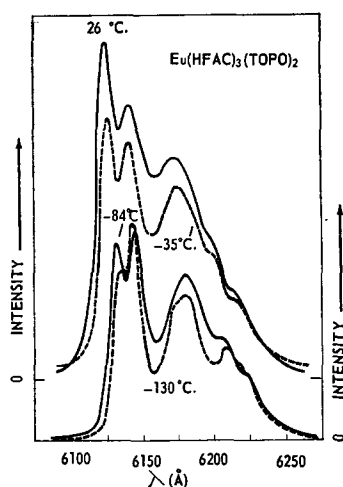FIG. 4. Luminescence spectrum of hydrocarbon (1:1 methylcyclohexane–3-methylpentane mixture) solution of Eu(HFAC)₃(DHSO)₂ at several temperatures.



FIG. 3. Luminescence spectrum of hydrocarbon (1:1 methylcyclohexane–3-methylpentane mixture) solution of Eu(HFAC)₃(TOPO)₂ at several temperatures.

room temperature, they diminish appreciably at low temperatures, and care must be taken to avoid formation of suspended crystallites.

Luminescence spectra of hydrocarbon solutions of various europium trifluoroacetylacetone complexes at room temperature are sketched in Fig. 5. The curves have been displaced relative to each other along the intensity axis for clarity in presentation.

## Luminescent Lifetime

Lifetimes were measured by recording the decay of luminescence intensity subsequent to excitation by a short flash of light. In all cases the decay was exponential, and so the lifetime was taken as the negative reciprocal of the mean slope of the intensity versus time. The decay was followed over two to three life-
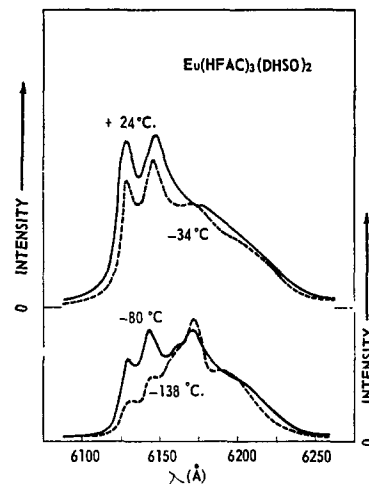
times, and the results were reproducible within about ±5%.

The equipment used is similar in concept to that described by Lindqvist,[14] and can be operated either to measure absorption of a standard monitoring light as a function of time during and subsequent to flash excitation, or to measure the intensity of emitted light as a function of time. The flashtubes are 18 mm in diameter, have an electrode spacing of 15 cm, and are connected to a gas line for filling. Using oxygen as the working gas, and a 5-μF capacitor charged to 25 000 V as the power source, the flash duration is about 25 μsec. A polymethylmethacrylate rod serves as a light pipe to activate a photomultiplier-pulse circuit for triggering the oscilloscope trace when the flashtubes fire. Light traveling along the optic axis of the flash excitation unit (either from the monitoring light or luminescence by the sample) is isolated by means of filters, lenses, and apertures before impinging on the
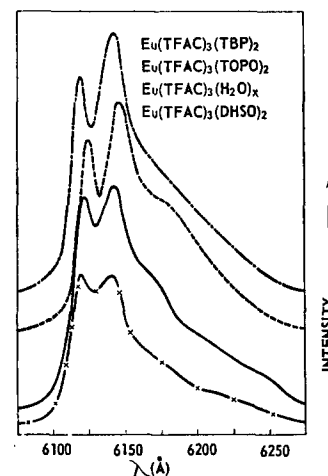


FIG. 5. Luminescence spectra of solutions of Eu(TFAC)₃ derivatives in the 6100 Å region at room temperature. Curves have been displaced vertically on the intensity scale for clarity. The Eu(TFAC)₃·(H₂O)ₓ spectrum is for an alcohol solution, while the remainder are hydrocarbon solutions (see text).

[12] J. G. Koren, J. S. Brinen, and R. C. Hirt (to be published).
[13] J. J. Freeman and G. A. Crosby, J. Phys. Chem. **67**, 2717 (1963).
[14] L. Lindqvist, Arkiv Kemi **16**, 80 (1960).

TABLE II. Luminescent lifetimes, $\tau_f$, and quantum efficiencies, $\Phi$.

| Compound | Solvent | Conc. | $T(°C)$ | $\tau_f(\mu sec)$ | $\Phi^a$ |
|---|---|---|---|---|---|
| Eu(AC)₃ | Alc. | $10^{-3}M$ | 25 | 226 | ... |
| Eu(AC)₃ | Hyd. | ? | 25 | 267? | ... |
| Eu(DPM)₃ | Alc. | $10^{-3}M$ | 25 | 310 | ... |
| Eu(DPM)₃ | Hyd. | ? | 25 | 326? | ... |
| Eu(TFAC)₃ | Alc. | $10^{-3}M$ | 25 | 435 | 0.044 |
| Eu(TFAC)₃ | Alc. | $10^{-3}M$ | −80 | ... | (0.15) |
| Eu(PFHD)₃ | Alc. | $10^{-4}M$ | 25 | 438 | 0.14 |
| Eu(PFHD)₃ | Alc. | $10^{-4}M$ | −80 | ... | (0.25) |
| Eu(PFHD)₃ | Hyd. | ? | 25 | 289? | ... |
| Eu(HFAC)₃ | Alc. | $10^{-3}M$ | 25 | 430 | 0.16 |
| Eu(HFAC)₃ | Alc. | $10^{-3}M$ | −80 | 460 | (0.24) |
| Eu(HFAC)₃ | Alc. | $10^{-3}M$ | −135 | 477 | (0.24) |
| Eu(DPM)₃(TOPO)₂ | Hyd. | $4×10^{-4}M$ | 25 | 487 | 0.028 |
| Eu(TFAC)₃(DHSO)₂ | Hyd. | $10^{-3}M$ | 25 | 463 | 0.13 |
| Eu(TFAC)₃(TBP)₂ | Hyd. | $5×10^{-4}M$ | 25 | 741 | 0.18 |
| Eu(TFAC)₃(TOPO)₂ | Hyd. | $10^{-3}M$ | 25 | 742 | 0.43 |
| Eu(PFHD)₃(TOPO)₂ | Hyd. | $10^{-3}M$ | 25 | 753 | 0.55 |
| Eu(HFAC)₃(DHSO)₂ | Hyd. | $5×10^{-4}M$ | 25 | 641 | 0.39 |
| Eu(HFAC)₃(TOPO)₂ | Hyd. | $10^{-3}M$ | 25 | 791 | 0.79 |
| Eu(HFAC)₃(TOPO)₂ | Hyd. | $10^{-2}M$ | 25 | ... | 0.70 |

ᵃ Quantum efficiencies in parentheses were obtained by multiplying the value at room temperature by the ratio of the areas under the luminescence curves at the indicated temperature and at 25°C.

entrance slit of a Perkin–Elmer monochromator. A red sensitive photomultiplier (DuMont 6292 or EMI 9554B) is mounted behind the exit slit of the monochromator, and the output passes through a cathode-follower amplifier to a Tektronix Model 531A oscilloscope.

The cells used are Pyrex or quartz cylinders about 12 mm i.d. and up to 15 cm long, closed at the ends with optically flat windows. Each cell is provided with one concentric jacket for circulating a cooling medium around the sample, and an outer evacuated jacket for insulation.

In general the samples were not degassed. One solution of Eu(TFAC)₃ in alcohol was subjected to five freeze–thaw cycles, with residual gas pumped off each time, and the sample cell then was sealed off under vacuum. The measured lifetime was the same as for the solution before degassing.

## Quantum Efficiency

Measurements of absolute quantum efficiencies were made only at room temperature. They involved use of a calibrated light source, a Bausch & Lomb grating monochromator, and a calibrated RCA 1P21 photomultiplier. Details of the equipment and the calibra-

tion are to be reported elsewhere.[15] Since the apparatus was designed for systems with broad emission bands, results for narrow band luminescence may be subject to an error as large as ±10%. As a check on the behavior of the equipment, a quantum efficiency of 0.18 for luminescence in the 6100-Å region was measured for an alcohol solution of a carefully purified sample of Eu(TTA)₃. This can be compared with the value 0.17–0.19[16] reported in the literature.[17]

The luminescence spectra at low temperatures permit an estimate of quantum efficiencies relative to room temperature for a given solution, by comparing the areas under the curves.

Data on quantum efficiencies are given in Table II. The concentrations listed refer to the direct measurement at room temperature.

## DISCUSSION

It is unfortunate that the true solubility of simple chelates in saturated hydrocarbon solvents is small, since the solvent then would represent a weakly bonded,

¹⁵ B. Roberts and R. C. Hirt (to be published).
¹⁶ The material used in the literature report was not the simple tris chelate but in an alcohol solution the luminescent species probably is the same, namely an alcoholate.
¹⁷ R. A. Gudmundsen, O. J. Marsh, and E. Matovich, J. Chem. Phys. **39**, 272 (1963).

poor electronic energy acceptor. It might be assumed, however, that such a constantly changing sheath would not provide the same protection toward quenching impurities as a permanently attached static sheath. Some tentative data on luminescence lifetimes for such solutions are given in Table II, but the concentrations were so small that the actual europium species present are questionable (might even be colloidal particles). Solution of synergic agent complexes in hydroxylic solvents, on the other hand, results in varying amounts of decomposition. Indeed, the use of ethylene glycol as a solvent results in virtually complete decomposition of $Eu(HFAC)_3(TOPO)_2$. Hence for solution studies of these materials the solvent is an integral part of the system, and in those situations where the solvent can coordinate with the lanthanide ion, the exact complex present in solution may be unknown.

The quantum efficiency for luminescence by europium tris acetylacetonate in alcohol solution is so small that an absolute value was not measured. While the same statement is applicable to the dipivaloylmethide chelate also, relative measurements show the latter to be greater by a factor of 20. In both cases the luminescent lifetime is long enough so that much of the radiationless loss must occur prior to storage of energy in the $^5D_0$ state. Since ligand energy levels are nearly the same, it is reasonable to ascribe the improvement in the dipivaloylmethide chelate to the bulky tertiary methyl groups as providing part of a sheath.

Another improvement occurs when the trifluoromethyl group is used in the insulating sheath, consistent with the known repulsive nature of perfluoro groupings. Extension of the sheath by the pentafluoroethyl and ethyl groupings (in europium tris pentafluoroheptadionate) provides further improvement in the quantum efficiency.

All of the alcohol solutions of these simple chelates exhibit an increase in quantum efficiency as the temperature is lowered, although the effect is diminished as the insulating sheath is improved via substituents. A considerable sharpening of structure is observed also, as illustrated in Fig. 2. Along with the improvement in quantum efficiency there is an increase in lifetime of the $^5D_0$ state with decreasing temperature.

A dramatic improvement in quantum efficiency and lifetime occurs at room temperature when the insulating sheath is completed by forming the synergic agent complex and then dissolving it in a hydrocarbon medium. In the cases cited in Table II there is a factor of 3 to 10 in quantum efficiency and 1.5 to 2.5 in lifetime. On an absolute basis, the absorption of broad-band radiation near 3000 Å and emission of narrow-band radiation near 6100 Å in a low-viscosity medium at room temperature with a quantum efficiency approaching 80% is remarkable.

The spectral intensity contour for room-temperature luminescence of a methylcyclohexane solution of a europium synergic agent complex is not strongly dependent on the choice of synergic agent (of the type described in the present article). This is illustrated by the curves in Fig. 5 for complexes of $Eu(TFAC)_3$, although a comparison of Figs. 3 and 4 show more of a change for $Eu(HFAC)_3$. In general coordination by hydroxylic solvents gives rise to a different appearance [$Eu(TFAC)_3$ is an exception], which may be a function of a multiplicity of emitting species.[11] Data are not available for deciding whether any appreciable difference in *radiative* lifetime of the $^5D_0$ state between the alcohol and hydrocarbon solutions is involved. Certainly the change in quantum efficiency is larger than the change in actual lifetime, and so a change in radiative lifetime is not required.

## CONCLUSIONS

The presence of an insulating sheath around the chelating-chromophore-europium ion moiety produces a major increase in the quantum efficiency of luminescence for room temperature low-viscosity solutions. In this way it is possible to achieve a quantum efficiency approaching 0.8 for narrow-band luminescence in the 6100 Å region.

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