

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231395703>

Nonparticipation of the Ligand's First Triplet State in Intramolecular Energy Transfer in Eu^{3+} and Tb^{3+} Ruhemann's Purple Complexes

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY · AUGUST 1995

Impact Factor: 2.78 · DOI: 10.1021/j100035a036

CITATIONS

21

READS

42

1 AUTHOR:



Ismail Mekkaoui Alaoui

Cadi Ayyad University

16 PUBLICATIONS 147 CITATIONS

SEE PROFILE

Nonparticipation of the Ligand's First Triplet State in Intramolecular Energy Transfer in Eu^{3+} and Tb^{3+} Ruhemann's Purple Complexes

Ismail Mekkaoui Alaoui

Physics Department, Faculty of Sciences Semlalia, University Cady Ayyad,
B.P. S15, Marrakech 40000, Morocco

Received: January 11, 1995; In Final Form: May 23, 1995[®]

In this paper, the participation of the ligand's first triplet state in intramolecular energy transfer in europium and terbium Ruhemann's Purple (RP) complexes is discussed. RP is the reaction product of ninhydrin and ninhydrin analogues with amino acids. A dual excitation experiment using an argon ion laser and a dye laser was conducted. This experiment does not support the participation of the ligand's first triplet state in intramolecular energy transfer in Eu –RP and Tb –RP complexes. The mechanism of intramolecular energy transfer in these complexes is also addressed. It seems that it is quite different from those known in the literature.

Intramolecular energy transfer (IMET) in europium and terbium Ruhemann's Purple (RP) complexes enhances the luminescence of the Eu^{3+} and Tb^{3+} ions. This luminescence enhancement is due to the intense and broad absorption peaks of the RP ligands in the near-ultraviolet and to the high quantum luminescence efficiency of the Eu^{3+} and Tb^{3+} ions. The preparation of the complexes, the conditions of the measurements, and the practical utilizations of these complexes are described in previous papers.^{1–5} The spectroscopic properties of Eu –RP and Tb –RP complexes are reported in refs 4 and 5, respectively. For simplicity, the ninhydrin and ninhydrin molecules and their abbreviations are as follows: ninhydrin, Nin; 5-methoxyninhydrin, 5MNin; benzo[f]ninhydrin, BNin; 5-methylthioninhydrin, 5MTNin; dihydrothiopheno[f]ninhydrin, DTPNin; 7-methoxybenzo[f]ninhydrin, 7MBNin. The following conventions will be adopted. (i) Let $S_{\lambda} \rightarrow S'_{\lambda'}$ be a given radiative transition, where λ and λ' are the orbital angular momentum contributions and S and S' are the spin of the initial and final state, respectively. It will be called fluorescence if $S = S'$, and phosphorescence if $S \neq S'$. (ii) A nonradiative transition will be represented by a wavy arrow, while a radiative transition will be represented by a straight arrow, \rightsquigarrow and \rightarrow , respectively.

Chemicals which develop latent fingerprints include non-fluorescent amino acid reagents. Ninhydrin and ninhydrin analogues, considered here, are among these chemicals. Several types of chemicals and procedures are available.^{6,7} Ninhydrin and ninhydrin analogues develop colored fingerprints which do not fluoresce visibly. If developed colored fingerprints require secondary treatments to render them visibly fluorescent, then complexation with ZnCl_2 is a routine procedure.⁸ Fluorescamine, *o*-phthalaldehyde, etc. develop invisible fingerprints which fluoresce visibly without any secondary treatment. Excitation in this case is usually in the ultraviolet (UV) region since the developed fingerprints are invisible and thus absorb only nonvisible radiation. DFO and some aminoninhydrin analogues develop colored fingerprints which fluoresce visibly without any secondary treatments.⁹ The use of rare earth (RE) salts is necessary when the background fluorescence overwhelms the fingerprints luminescence.^{1,2} Treatment of ninhydrin and ninhydrin analogues developed fingerprints with europium (terbium) salts form the Eu –RP (Tb –RP) complexes. These

complexes show emission enhancement of the RE ions, via IMET from the RP ligands to the ions Eu^{3+} (Tb^{3+}) when excited in the near-UV region. Since the emission lifetimes of the Eu^{3+} and Tb^{3+} ions are in the millisecond order and most surfaces' fluorescence is in the nanosecond order, the background fluorescence is suppressed by means of time-resolved luminescence imaging technique, and fingerprints luminescence is nicely detected.⁴

The probability^{10,11} that the energy is transferred from a donor D to an acceptor A is of the form

$$P_{\text{DA}} \propto \left| \int \Psi_i^* H' \Psi_f d\tau \right|^2$$

where H' is the perturbation Hamiltonian and Ψ_i and Ψ_f are the initial and final wave functions. H' is the sum of the electric interactions. $H' = \text{dipole-dipole} + \text{dipole-quadrupole} + \text{higher interactions}$. Knowing the wave functions of the system at the initial state and the final state will make the problem approachable, though tedious, but possible in the case of weak perturbations and linear molecules.¹² In the case of Eu –RP and Tb –RP complexes, the problem is complex, because not only the RP are excited by UV radiation but Eu^{3+} and Tb^{3+} themselves are also excited. The wave functions are not easily approachable. The transitions in rare earths are forbidden (*f*–*f*), and consequently dipole–dipole transitions are not likely to be operative and higher order interactions are going to be involved in the perturbation Hamiltonian. Calculations are lengthy and involve a large number of potential energy transfer mechanisms. For the above-mentioned complications and for practical aspects, this problem is treated from experimental observations. To understand the mechanism by which the energy is transferred from the RP ligands to the lanthanide ions Eu^{3+} and Tb^{3+} , the energy-level scheme has been derived from absorption and emission spectra at room temperature.

Prelude to IMET in Rare Earth Chelates

The phenomenon of IMET in RE chelates was first reported by Weissman,¹³ who studied chelates of Eu , Sm , and Tb with various ligands. He concluded that the excitation light is absorbed by the organic part of the lanthanide complex and emitted as the line spectrum of the lanthanide ion. A mechanism of IMET in some RE chelates was published by Crosby et al.^{14–16} It involves the participation of the first excited singlet

[®] Abstract published in *Advance ACS Abstracts*, August 1, 1995.

TABLE 1: Absorption Peaks (nm) of 10^{-5} M Methanol Solutions of Eu-RP Complexes, in the 200–800 nm Range, at Room Temperature

Eu-RP(Nin)	230; 260; 364; 406; 504
Eu-RP(5MNin)	232; 364; 394; 416; 516
Eu-RP(BNin)	234; 270; 314; 364; 446; 548
Eu-RP(7MBNin)	228; 256; 278; 330; 414; 562
Eu-RP(5MTNin)	210; 246; 314; 398; 534
Eu-RP(DTPNin)	208; 242; 272; 314; 422; 538

TABLE 2: Absorption Peaks (nm) of 10^{-5} M Methanol Solutions of Tb-RP Complexes, in the 200–800 nm Range, at Room Temperature

Tb-RP(Nin)	208; 238; 368; 420; 502
Tb-RP(5MNin)	244; 282; 364; 416; 514
Tb-RP(BNin)	238; 270; 318; 364; 452; 542
Tb-RP(7MBNin)	212; 254; 278; 328; 414; 566
Tb-RP(5MTNin)	210; 318; 412; 534; 572
Tb-RP(DTPNin)	242; 272; 314; 364; 422; 538

(S_1) and triplet (T_1) states of the ligands. This IMET scheme was based on the observation that sensitized lanthanide emission occurs for chelates whose triplet states lie above the emitting lanthanide level, but not for chelates whose triplet states are below this level. Kleinerman^{17,18} pointed out that the theory of Crosby et al. is not conclusively supported by evidence and, in some RE chelate systems, the IMET process seems to proceed through an inductive resonance mechanism connecting a ligand-excited singlet level and a RE ion level higher than the emissive one, which is a direct IMET from the ligand's first singlet state to the RE ions. Bhaumik and El-Sayed¹⁹ and Kazanskaya et al.²⁰ supported the involvement of the triplet state in the IMET mechanism in the RE chelates they studied. Matsuda et al.²¹ reported also that IMET in europium dibenzoylmethide takes place via the triplet state of the ligand.

The scheme given by Crosby et al. does not seem to work in the case of Eu-RP and Tb-RP complexes. In the Eu-RP complexes, the ligand's first excited state (Table 1) is above the emissive 5D_0 level of Eu^{3+} (about $18\,000\text{ cm}^{-1}$), but no IMET is seen when using the 488 nm ($20\,300\text{ cm}^{-1}$) line of the argon laser as excitation of the Eu-RP samples. In the Tb-RP complexes, the ligand's first singlet excited state S_1 (Table 2) is below the emissive 5D_4 level of Tb^{3+} (about $21\,000\text{ cm}^{-1}$). No energy can be transferred from a low energy level to a higher energy level for energy considerations. This line is above the first singlet state of the Tb-RP ligands. There is also no evidence of the participation of the triplet state in IMET as explained in details in the last section of this paper. A dipole-dipole mechanism, such as the Forster^{22,23} process, is not likely to be operative, being parity-forbidden. Intramolecular energy transfer via forbidden transitions may be allowed by exchange interactions.²⁴ Kleinerman's salient conclusion that ligand-RE IMET can be explained by direct transfer from the ligand's first excited singlet state to the ions does not hold for either the Eu-RP nor the Tb-RP complexes.

Energy Transfer from the RP Ligands to Eu^{3+}

Indeed there are a variety of mechanisms by which IMET can take place, even from higher excited states, including charge transfer, dipole-quadrupole interactions, and exchange mechanisms. Figure 1 represents the energy levels scheme of Eu-RP derived from absorption and emission spectra of these complexes and that of Eu^{3+} as reported by DeShazer and Dieke.²⁵ Let us first give two important experimental observations.

Excitations with an argon ion laser working in the visible (all lines) of Eu-RP samples on thin layer chromatography

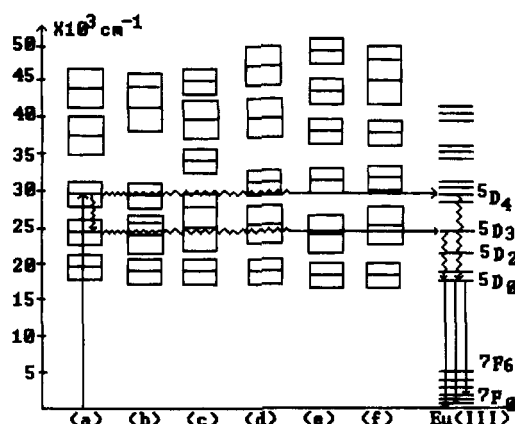


Figure 1. Energy levels of Eu-RP complexes and E(III): (a) Eu-RP(Nin); (b) Eu-RP(5MNin); (c) Eu-RP(BNin); (d) Eu-RP(5MTNin); (e) Eu-RP(DTPNin); (f) Eu-RP(7MBNin). Possible path of energy transfer from the ligands to the Eu(III) ion.

(TLC) plates and in solutions at room temperature do not lead to any ion phosphorescence, even though the ligands absorb in the visible⁴ (at 504 nm for Eu-RP(Nin) for example), and the emitting level 5D_0 (579 nm) of Eu^{3+} is below those levels.

If $S_1 \rightsquigarrow \text{RE}$ energy transfer via dipole-dipole or dipole-quadrupole coupling were operative, then enhanced emission of Eu-RP(7MBNin) or Eu-RP(BNin), where the overlap between the Stokes-shifted S_1 level and the emissive 5D_0 level of Eu^{3+} (at 579 nm) is good, should be obtained under dye laser excitation in the 550–580 nm range. One should point out here that Eu^{3+} by itself is excited under 579 nm radiation $^5D_0 \leftarrow ^7F_0$ at $17\,277\text{ cm}^{-1}$. Again, no enhanced emission of any Eu-RP complexes was found under such excitation.

In the Eu-RP complexes, the IMET proceeds then by $S_n \rightsquigarrow \text{RE}$, or $T_n \rightsquigarrow \text{RE}$, where S_n and T_n denote a higher excited ligand singlet or triplet state. Cascading from the higher RE states then takes place down to the emitting level 5D_0 . In the case of RP ligands, part of the energy ($25\,000$ – $39\,000\text{ cm}^{-1}$) absorbed by the complexes's second or third excited singlet state is transferred directly to the neighboring 5D_2 or 5D_3 4f levels of Eu^{3+} via nonradiative transitions. The energy is then transferred to the 5D_1 and 5D_0 emitting levels from which Eu^{3+} undergo radiative transitions (ion phosphorescence) to the 7F multiplet. The radiative transitions from 5D_1 are very weak and superposed in the region of the strong $^5D_0 \rightarrow ^7F_2$ region, they are not seen in Eu-RP complexes at room temperature conditions.

Energy Transfer from the RP Ligands to Tb^{3+}

The Tb-RP cases are different from the Eu-RP cases in the sense that the first excited singlet states of the Tb-RP complexes (502 nm for Tb-RP(Nin), 514 nm for Tb-RP(5MNin), etc.) are below the emissive level 5D_4 (488 nm) of Tb^{3+} . That means that no energy transfer can occur from the RP ligand's first excited singlet state to the Tb's emitting 5D_4 energy level. We need to excite the ligand's higher states to possibly have energy transferred to one of the Tb^{3+} levels. But except for these differences, the energy transfer in Tb-RP seems to proceed via similar steps as in Eu-RP cases. Figure 2 shows the energy levels scheme of Tb-RP complexes derived from absorption and emission spectra, at room temperature,⁵ and that of Tb^{3+} as reported by Thomas et al.²⁶

Tb-RP(BNin) shows enhanced Tb^{3+} luminescence under near-ultraviolet excitation, much like Eu-RP(BNin). In this complex the absorption band corresponding to the $S_0 \rightarrow S_1$ transition lies at 542 nm, corresponding to an energy of about

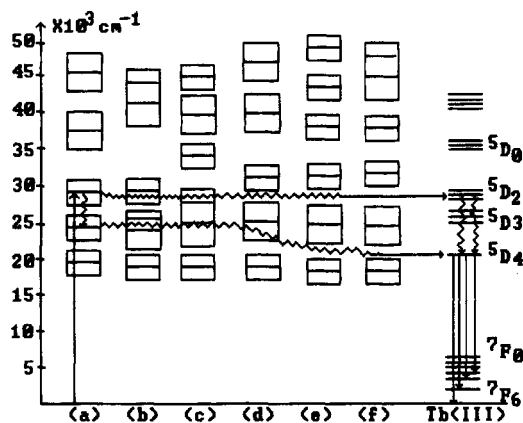


Figure 2. Energy levels of Tb-RP complexes and Tb(III): (a) Tb-RP(Nin); (b) Tb-RP(5MNin); (c) Tb-RP(BNin); (d) Tb-RP(5MTNin); (e) Tb-RP(DTPNin); (f) Tb-RP(7MBNin). Possible path of energy transfer from the ligand to the Tb(III) ion.

$18\,400\text{ cm}^{-1}$. The $7F_6$ (ground state)– $5D_4$ (emitting state) energy gap for Tb^{3+} is $20\,400\text{ cm}^{-1}$. The first excited singlet state of the ligand (S_1) and therefore also the lowest triplet state (T_1) both lie below the emitting $5D_4$ level, and yet sensitized emission takes place. Clearly, a higher excited ligand state is involved in the energy transfer process. Indeed, our results indicate that in the RE-RP complexes the positions of S_1 and T_1 are of no relevance to speak of. For instance, Tb-RP(Nin), which shows sensitized Tb^{3+} luminescence under near-ultraviolet excitation, has the $S_0 \rightarrow S_1$ absorption band at 502 nm. The absorption band is broad, having considerable overlap with the $7F_6$ – $5D_4$ transition. If a resonance-type mechanism involving S_1 were operative, then one would expect to observe sensitized Tb^{3+} luminescence under excitation by an Ar laser light at 488 nm. This was not found. None of the Tb-RP complexes showed any enhanced emission under blue-green argon ion laser excitation, which rules out $S_1 \rightsquigarrow T_1 \rightsquigarrow Tb^{3+}$ energy transfer.

The UV radiation absorbed by the ligands of the complexes ($26\,000$ – $39\,000\text{ cm}^{-1}$) is transferred via nonradiative transitions to high $4f^8$ levels and then to the $5D_4$ emitting energy level of Tb^{3+} from which the ion undergoes ion's phosphorescence to the $7F_j$ multiplet. The efficiency of the IMET seems to be much better for the Eu-RP complexes than for the Tb-RP complexes, in general. In the Eu-RP and Tb-RP complexes the IMET proceeds by $S_n \rightsquigarrow RE$, or $T_n \rightsquigarrow RE$, where S_n and T_n denote a higher excited ligand singlet or triplet state. Cascading from the higher RE states then takes place down to the emitting levels. The possibility of the participation of the first excited triplet state is discussed in the following section.

Energy Transfer via the Ligand's First Triplet State

The probability of excitation of the triplet states (T_n) of the ligand due to direct optical absorption from the ground state is extremely small if not impossible. To investigate whether T_n is involved in the energy transfer ($S_n \rightarrow T_n \rightarrow RE$), a dual excitation experiment was conducted. The first excitation source was blue-green Ar laser excitation, with high power (about 20 W). It produces T_1 via $S_1 \rightsquigarrow T_1$ intersystem crossing. In RP ligands, intersystem crossing is expected to be efficient since no appreciable ligand fluorescence is observed in most of the ligands, unlike in the corresponding zinc complexes.²⁷ The second excitation (either an Ar laser operating in the blue-green or a dye laser operating from yellow (about 560 nm) to red (about 620 nm)) source produces T_n via T_1 – T_n triplet–triplet absorption. T–T absorption was observed in Eu, Tb, and other RE complexes.²⁸ The samples were Eu-RP and Tb-RP

spotted on TLC plates and in solution at room temperature. Although the location of the T_1 level in these samples is not known, one can safely assume that it must be somewhere between 600 and 1000 nm. We therefore have ample photon energies via the second excitation to reach T_n (at about 350 nm) from T_1 , or a higher triplet level from which T_n is reached via internal conversion. The signals from the samples were recorded by a boxcar averager. No Eu^{3+} or Tb^{3+} emissions were observed at room temperature in any of the TLC nor the solutions samples, suggesting that T_n is not involved in the sensitized europium or terbium emission process in Eu-RP and Tb-RP complexes.

Conclusion

The mechanism of IMET in these complexes is quite different than the proposed IMET mechanism in the previous europium and terbium chelates studied in the literature. The experiments conducted, at room temperature conditions, show that it proceeds via an upper excited state, most likely a singlet, of the chelate, most probably via a dipole–multipole interaction. The results of the dual excitation experiment do not support the possibility of the participation of the triplet state in IMET in the case of Eu-RP and Tb-RP chelates.

Acknowledgment. Most of this work was done at the physics department, Texas Tech University. I am indebted to Professor Roland E. Menzel, Director of the Center for Forensic Studies, for his assistance with these experiments.

References and Notes

- (1) Mitchell, K. E.; Menzel, E. R. *Fluores. Detec. III, SPIE Proc.* **1989**, 1054, 191.
- (2) Menzel, E. R.; Mitchell, K. E. *J. Forensic Sci.* **1990**, 35, 35.
- (3) Mekkaoui Alaoui, I.; Menzel, E. R. *Bull. Am. Phys. Soc. Ser. 2* **1992**, 37, 1083.
- (4) Mekkaoui Alaoui, I.; Menzel, E. R. *J. Forensic Sci.* **1993**, 38, 506.
- (5) Mekkaoui Alaoui, I.; Menzel, E. R. *J. Forensic Sci. Int.* **1994**, 66, 203.
- (6) Sasson, C. A.; Almog, J. *J. Forensic Sci.* **1978**, 23, 852.
- (7) Almog, J.; Hirshfeld, A.; Klug, A. T. *J. Forensic Sci.* **1982**, 27, 912.
- (8) Herold, D. W.; Menzel, E. R. *J. Forensic Sci.* **1982**, 27, 513.
- (9) Almog, J.; Hirshfeld, A.; Frank, A.; Sterling, J.; Leonov, D. *J. Forensic Sci.* **1991**, 36, 104.
- (10) Saxon, D. S. *Elementary Quantum Mechanics*; Holden-Day Inc.: San Francisco, 1968; Chapter 7.
- (11) Schiff, L. I. *Quantum Mechanics*; McGraw-Hill: New York, 1949; Chapter 4.
- (12) Reviejo, M. M.; Nunez, M. F. *An. Quim.* **1991**, 87, 311.
- (13) Weissman, S. I. *J. Chem. Phys.* **1942**, 10, 214.
- (14) Crosby, G. A.; Whan, R. E.; Alire, R. M. *J. Chem. Phys.* **1961**, 34, 743.
- (15) Crosby, G. A.; Whan, R. E.; Freeman, J. J. *J. Phys. Chem.* **1962**, 66, 2493.
- (16) Whan, R. E.; Crosby, G. A. *J. Mol. Spectrosc.* **1962**, 8, 315.
- (17) Kleinerman, M. *Bull. Am. Phys. Soc.* **1964**, 9, 26.
- (18) Kleinerman, M. *J. Chem. Phys.* **1968**, 51, 2370.
- (19) Bhaumik, M. L.; El-Sayed, M. A. *J. Chem. Phys.* **1965**, 42, 787.
- (20) Kazanskaya, N. A.; Ermolaev, V. L.; Moshinskaya, A. V.; Petrov, A. A.; Kheruze, Y. L. *Opt. Spectrosc.* **1970**, 28, 619.
- (21) Matsuda, Y.; Makishima, S.; Shionoya, S. *Bull. Chem. Soc. Jpn.* **1968**, 41, 1513.
- (22) Fhorster, Th. *Ann. Phys.* **1948**, 2, 55.
- (23) Fhorster, Th. *Faraday Soc. Discuss.* **1959**, 27, 7.
- (24) Levy, S.-T.; Speiser, S. J. *J. Chem. Phys.* **1992**, 56, 3585.
- (25) DeShazer, L. G.; Dieke, G. H. *J. Chem. Phys.* **1963**, 38, 2190.
- (26) Thomas, K. S.; Singh, S.; Dieke, G. H. *J. Chem. Phys.* **1963**, 38, 2180.
- (27) Menzel, E. R.; Bartsch, R. A.; Hallman, J. L. *J. Forensic Sci.* **1990**, 35, 25.
- (28) Tsvirko, M. P.; Solov'ev, K. N.; Piskarskas, A. S.; Pyatosin, V. E.; Krasauskas, V. V.; Kachura, T. F. *Sov. Phys.-Dokl.* **1984**, 29, 1028.