

SYNTHESIS, CHARACTERIZATION AND ENERGY TRANSFER FLUORESCENCE OF EUROPIUM (III) IN CHELATE COMPLEXES*

Gilberto F. de Sá e Fabiana R. Gonçalves

Departamento de Química Fundamental – CCEN – Cidade Universitária – 50739 – Recife – PE

Recebido em 28/06/91

We have investigated the synthesis, characterization and some photophysical properties of the chelate complexes of Eu (III) with 2-pyrazine carboxylic acid and 2,2-bipyridine or 1,10-phenantroline. The complexes were characterized by means of chemical analysis, IR, lifetime, excitation and emission spectra. They are efficient luminophores which behave as light absorbers, through the ligand groups, and red emitters via efficient intramolecular energy transfer to Eu (III).

1. INTRODUCTION

In a previous work¹ we described the synthesis and structural characterization of the complexes formed between the lanthanoid ions and 2-pyrazine carboxylic acid.

The present work deals with the synthesis, characterization, and some spectroscopic and photophysical properties of chelate complexes of Eu (III) with 2-pyrazine carboxylic acid (Hpya) and two other ligands [1,10-phenantroline (phen) or 2,2'-bipyridine (bipy)] which behave as light absorbers (photosensitizers).²

The ability of some lanthanoid ions to fluoresce in solution or solid compounds at room temperature allows a broad amount of structural information to be obtained. In particular Eu (III) and Tb (III) have been used extensively as structural probes in fluorescence studies^{3, 4}. It is well known⁴ that Eu (III) is the more desirable owing to its nondegenerate ground (7F_0) and first excited (5D_0) state. Since neither the ground state nor the first excited 5D_0 state can be split by the ligand field, a single electronic transition is observed for each distinct Eu (III) environment.

2. EXPERIMENTAL PROCEDURE

The chelate complexes were prepared in essentially the same way as described previously.^{6,7} To a warm aquo-ethanolic solution containing 3.3 mmol of HL was gradually added an aqueous suspension containing 1.0 mmol of the europium basic carbonate. The solution cleared and after reduction of the volume was added an ethanolic solution containing 1.0 mmol of bipy or phen in the presence of triethyl orthoformate. The product thus isolated could not be recrystallized owing to lack of solubility in suitable solvents; however, it was filtered out with suction, washed on the filter with hot methanol, and dried at 90°C over P₂O₄ in an Abderhalden drying apparatus.

The elemental analysis for carbon, hydrogen, and nitrogen of the compounds were performed by the microanalytical Laboratory of the University of São Paulo. Experimental data are in good agreement with the theoretical values (Found: C, 44.02; H, 2.48; N, 16.71. Calc. for [Eu (pya)₃bipy]: C, 44.32; H, 2.53; N, 16.54%) and (Found: C, 45.92; H, 2.50; N, 16.10. Calc. for

[EuL₃.phen]: C, 46.23; H, 2.45; N, 15.98%).

The infrared spectra obtained on mulls (Nujol and Fluorolube) and on KBr pellets were taken in the region 4000-650 cm⁻¹ with a Beckman 4220 Spectrophotometer. The excitation and fluorescence spectra were excited with a 150 W xenon lamp, followed by a 0.25 m halographic grating monochromator (Jobin Yvon minimate) for wavelength selection. The fluorescence spectra were obtained with a Jobin Yvon double monochromator "Ramanor U 1000", with a slit width of 100 μm. The fluorescence following excitation was detected by a water-cooled RCA C31034-02 photomultiplier, and the signal was processed by a Jobin Yvon spectralink acquisition data. Fluorescence lifetime⁷ measurements were performed at 298 K, using a nitrogen laser exciting radiation at 337 nm.

3. RESULTS AND DISCUSSIONS

The reaction between the europium basic carbonate and 2-pyrazine carboxylic acid in the presence of one mmole of bipy or phen results in the formation of solid yellowish compounds. These compounds are finely divided powders which decompose at temperatures between 340 and 360°C without melting.

The compounds [Eu(pya)₃bipy] and [Eu(pya)₃phen] were characterized by means of elemental analysis, infrared, excitation and fluorescence spectra.

The hardness of the lanthanoid would be expected to favour coordination to oxygen. In the free ligand the relevant IR bands are a strong one at 1710 cm⁻¹ and two broad ones of medium intensities at 2450 and 1900 cm⁻¹. The band generally assigned to the antisymmetric carbonyl stretch in the COOH group^{6, 9} is absent in the spectra of the complexes. This strong band is replaced by a very strong one centered at 1610 – 1625 cm⁻¹ which is the antisymmetric stretching mode of the coordinated carboxylate.^{9, 10} The presence of the 2450 and 1900 cm⁻¹ bands in the free ligand indicates that it exists as a monomeric species¹. In complexes, the spectra are characteristic of chelate ring formation, with binding of the ligands (pya) to the lanthanoid through the nitrogen atom and the COOH group.^{10, 11}

The fluorescence spectra of [EuL₃.bipy] and [EuL₃.phen] in the solids at 298 K show high similarity. The results obtained from the analysis of the fluorescence spectra of [EuL₃.bipy] complex are shown in table 1 along with the suggested assignments of the $^5D_0 \rightarrow ^7F_{0, 1, 2}$ transitions. The

* Dedicado ao Prof. Ernesto Giesbrecht, por ocasião dos seus 70 anos.

Table 1 – Allowed transitions between selected states in D_{4d} , D_{2d} , and D_2 symmetries.

Transition	D_{4d}	D_{2d}	D_2	Eu(py ₃) ₃ bipy Assignments (nm)		
$^5D_0 \rightarrow ^7F_1$	$A_1 \rightarrow A_2$	$A_1 \rightarrow A_2$	$A \rightarrow B_2$	590.7	592.0	594.8
		$A_1 \rightarrow E$	$A \rightarrow B_2$			
			$A \rightarrow B_3$			
$^5D_0 \rightarrow ^7F_2$	$A_1 \rightarrow E_2$	$A_1 \rightarrow B_2$	$A \rightarrow B_1$	613.9	617.8	618.4
		$A_1 \rightarrow E$	$A \rightarrow B_2$			
			$A \rightarrow B_3$			

most intense transition is the $^5D_0 \rightarrow ^7F_2$, followed by $^5D_0 \rightarrow ^7F_1$ and by a very weak $^5D_0 \rightarrow ^7F_0$. The $^5D_0 \rightarrow ^7F_0$ ($\approx 5796 \text{ \AA}$) transition is strictly forbidden in D_2 symmetry if it is considered to be of electric dipole origin, which has already been discussed¹². In fact, the inclusion of J mixing to evaluate the matrix elements of the pseudo-quadrupolar interaction¹⁹ may be of great value in interpreting the $^5D_0 \rightarrow ^7F_0$ intensity as observed in the present work.

Usually, the dominant geometries for eight coordination complexes are those derived from the square anti-prism (D_{4d}) or the dodecahedron (D_{2d})¹⁴. Both can give rise to structures that possess D_2 symmetry. The fluorescence spectrum is in agreement with what would be expected for Eu^{3+} in a D_2 environment but unfortunately it is not possible to choose between the structure which is derived from the antiprism and that which is derived from the dodecahedron. The lifetimes of the 5D_0 excited state under various experimental conditions, obtained from fluorescence decay measurements, are shown in table 2, where the lifetime of Eu^{3+} (aquo) is also reported for comparison. The fluorescence lifetimes of the new europium complexes (table 2) are about five times larger than in the case of aqueous ion (110 μs) and than in the case of the [Eu(py₃)₃.2H₂O] complex (210 μs). It is well known that the deactivation of 5D_0 level of the Eu^{3+} is strongly enhanced by coupling with the OH vibration¹⁶. This is the reason why the excited-state lifetime of Eu^{3+} (aquo) is much shorter than that of Eu(py₃)₃bipy or Eu(py₃)₃phen (table 2). Further, this also may be due, at least in part, to a better shielding of the Eu (III) by the bipy or phen sensitizers and by the other ligands.

Table 2 – Photophysical properties of mixed complexes of Eu (III). [a], [b] and [c].

	Lifetimes	Linewidth	λ_{em}
	(μs)	$^5D_0 \rightarrow ^7F_0$ (nm)	(nm)
Eu(py ₃) ₃ 2H ₂ O	210	0.45	617
Eu(py ₃) ₃ bipy	639	0.38	617
Eu(py ₃) ₃ phen	525	0.39	617
Eu^{3+} (aquo) ^b	110	–	–
EuL ₃ . bipy ^c	334	0.41	615

[a] – All measurements were performed at 298 K by a nitrogen laser exciting at 337 nm (Ref. 7); Lifetimes $\pm 20\%$.

[b] – Eu(ClO₄)₃ . 6H₂O, 1.0 . 10⁻²M (Ref. 15).

[c] – Ref. 2.

4. CONCLUDING REMARKS

We have found that these new compounds show very intense fluorescence making them efficient light-conversion molecular devices, similar to those recently described by Lehn². It is important to emphasize that they also have the advantage of being simpler than the devices obtained with cryptates of macrobicyclic². In addition, these compounds are of interest as novel fluorescent materials in the solid state and as labels for biological applications such as time-resolved luminescence immunoassays employing monoclonal antibodies, oligonucleotides or cytofluorometry^{2,3,16-18}.

ACKNOWLEDGEMENTS

Financial support by the CNPq, CAPES, PADCT and FINEP (Brazilian Agencies) is gratefully acknowledged. We are also grateful to prof. Oscar L. Malta and Walter M. de Azevedo for helpful discussion.

REFERENCES

- de Sá, G.F.; Neto, B. de B.; Ferreira, R.; *Inorg. Chim. Acta.*, (1977), **23**, 249.
- Lehn, J.M.; *Angew. Chem. Int. Ed. Engl.* (1990), **24**, 1304, and references cited therein.
- Richardson, F.S.; *Chem. Rev.* (1982), **82**, 541.
- Horrocks Jr.; W. Dew; Sudnick, D.R.; *Accounts Chem. Res.*(1981), **14**, 384.
- de Sá, G.F.; *Polyhedron*, (1983), **2**, 1057.
- de Sá, G.F.; Giesbrecht, E.; Thompson, L.C.; *J. Inorg. Nucl. Chem.*, (1975), **37**, 109.
- We thank prof. Anderson Gomes for assistance with the lifetime measurements.
- Hakamoto, K.; Morimoto, Y.; Martell, A.E.; *J. Am. Chem. Soc.*, (1962), **84**, 2081.
- Hakamoto, K.; *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; John Wiley – Sons; New York, (1986).
- Bennetollo, F.; Bombiere, G.; Fonda, K.K.; Polo, A.; Quagliano, J.R.; Vallarino, L.M.; *Inorg. Chem.*, (1991), **30**, 6, 1345.
- de Sá, G.F.; Neto, B.B.; Ferreira, R.; *Inorg. Chim. Acta.*, (1977), **23**, 201.
- Malta, O.L.; *Molec. Phys.* (1981), **42**, 65.
- Malta, O.L.; de Sá, G.F.; *Chem. Phys. Lett.* (1980), **74**, 101.
- Matterties, E.L.; Wright, C.M.; *Quart Rev.* (1967), **21**, 109.
- Blasse, G.; Remmler-Sack, S.; *Ber. Bunsenges. Physik. Chem.* (1983), **87**, 352.
- Horrocks, W. Dew.; Sudnick, D.R.; *Acc. Chem. Res.*, (1981), **14**, 384.
- Horrocks Jr., W.; *Prog. Inorg. Chem.*, (1984), **31**, 1.
- Marshall, N.J.; Dakubu, T.; Ekins, R.P.; Albertini (Eds.) : "Monoclonal Antibodies and Developments in Immunoassay". Elsevier / North – Holland Biomedical Press, Amsterdam, (1981), p. 101.