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Multifunction coordinative compounds of Er (III) based on azo-derivatives and Schiff bases ligands as chromophores in non-linear optics

A. EMANDI*, C. VASILIU[a], M. VASILESCU[b], M. VOICESCU[b], R. BANDULA[b]
University of Bucharest, Faculty of Chemistry, Department of Inorganic Chemistry, Str. Dumbrava Rosie nr 23, Sector 2, Cod 010184, Bucharest, Romania
[a]*National Institute of of Research and Development for Optoelectronics-INOE 2000, Department of Optospintronics, Atomistilor Str. 1, P.O.Box MG - 5, RO-77125, Com.Magurele, Romania*
[b]*Institute of Physical Chemistry, Romanian Academy, Splaiul Independentei 202, 006021 Bucharest, Romania*

A series of Er(III) six-coordinated complexes with the general formulae $[Er(LH)_3]$ of the tridentate ligands (LH_2) were obtained for the metal to ligand ratio 1/3. Chelates prototype complexes based on azo-derivatives and Schiff bases as ligands were characterized by elemental analyses and FTIR methods. Luminescence properties and the antenna effect of the organic ligands were investigated. The aim of syntheses and characterization of these multifunctional materials was to use them as fiber amplifiers in optoelectronic devices.

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1. Introduction

Growing demand for the exchange of information in commerce, education, health, government, security, and entertainment creates immense need for transmission bandwidth [1].

Optical fiber provides a suitable medium in which it is possible to reach tremendous transmission rates over long distances using a combination of wavelength - and time - division multiplexing. Optical devices such as arrayed waveguide gratings, micro-electro-mechanical systems (MEMS), fiber Bragg gratings, erbium-doped fiber amplifiers, and isolators are used to multiplex and de-multiplex signals, perform coarse switching, amplify pulses, and control the direction of the light flow [2]. At present, important, functionally complex operations such as regeneration, reshaping, retiming, and packet routing are carried out electronically. Optical pulses must be converted to electrical signals, processed in the electronic domain, and then converted back to the optical domain. Both the processes of optical-electronic-optical conversion, and also the electronic signal processing itself, give rise to bottlenecking at switching and regeneration nodes in present-day optical high-capacity networks. The ability to perform information processing operations entirely within the optical domain would eliminate the need for opto-electrical-opto conversion. The speed of electronic devices would no longer limit network throughput: optical signal processing, in contrast with electronics, may provide subpicosecond switching periods. In an optical switch, light interacts with light by means of a nonlinear material [3].

Luminiscent lanthanide complexes consist of a lanthanide ion as photonic active component and its chelating luminescent ligands as sensitizers which can transfer excitation energy from the ligand to the lanthanide cation are very interesting. However, luminescent lanthanide complexes were not developed in specific reference to advanced photonic materials by now. They are simply supramolecular complexes containing well known antenna chromophores to photoexcite the lanthanide ions *via* the energy transfer process. Optical communication wavelength is around 1.3 μm and the finding of advanced photonic media with good stability in time containing lanthanide ions as a carrier of information at this wavelength is just in the early stage.[4,5]

We attempted to synthesize very stable in normal conditions Er(III) chelated complexes based on luminescent azoderivatives and Schiff bases as ligands in order to investigate important parameters for emission enhancement.

2. Experimental

Dihydroxyazobenzene and erbium azotate were of AnalaR grade.

The Schiff bases were synthesized in our laboratory by the method [6].

To a hot solution of ligand (0.6mM) in EtOH, an ethanol solution of the metal nitrate (1.8mM) was added and the mixture was stirred and refluxed for 1.5 h on a water bath till the complex precipitated out. The pH of the solution was adjusted with ammonia solution up to 7-7.5

during the reaction. A fine crystalline product was separated on cooling. It was filtered, washed with EtOH .

Carlo Erba EA 1108 equipment was used for elemental analyses.

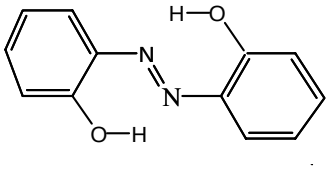
IR spectra were recorded on a Perkin Elmer SPECTRUM 100 spectrometer in the range 550-4000 cm^{-1}. All spectra were obtained using a UATR accessory with a resolution of 8 cm^{-1}, 16 scans and a CO_2/H_2O correction.

Luminescent properties were evaluated using a Spectrofluorimeter Perkin Elmer 204, Range 220-780 nm; spectral fixed bandwidth of 5 nm. For UVVIS spectra a UV-VIS Lambda 35, 200 – 1500 nm spectrophotometer was used.

3. Results and discussion

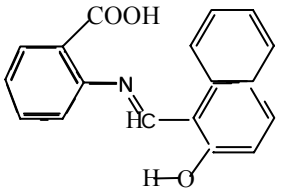
In order to investigate important parameters for emission enhancement our work was focused on a systematic study regarding the synthesis of a series of azoderivative and Schiff bases coordination compounds of Er(III) cation by hindering the –N=N– and respectively –CH=N– groups. The study began with a very simple tridentate azoderivative dihydroxy azobenzene (DAB) with the following formulae:

o, o` - dihydroxi azobenzene (DAB)

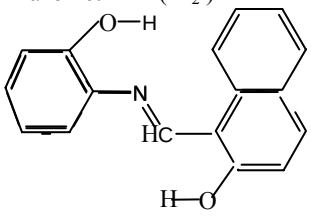


and two schiff bases n-(2-hydroxy-1-naphthalidene) amino phenole D_2 and n-(2-hydroxy-1-naphthalidene) anthranilic acid D_3 with the following formula**:**

o, - hydroxi - o` - carboxy azomethin (D_3)



o, o` - dihydroxi azomethin (D_2)



The analytical data along with some physical properties of the complexes are summarized in table 1. The tridentate, dibasic ligands LH_2, on interaction with Er(III) nitrate yields complexes corresponding to the general formula $[Er(LH)_3]$ where LH = (DAB), (D_2), (D_3) as mono-de-protonated ligands.

The analytical data show that the metal to ligand ratio is 1:3. They are soluble in common organic solvents. The low molar conductance values of complexes reveal their non-electrolytic nature.[7]

Table 1. Physical characteristic and analytical data of the complexes.

Compounds	λ_m (nho.cm^{-2}.mol^{-1})	Yield (%)	Analysis, found (calcd) (%)		
			C%	N%	M%
$[Er(DAB)_3]$	12.16	60	67.00(67.28)	13.00(13.08)	26.00(26.16)
$[Er(D_3)_3]$	11.15	56	64.20(64.47)	4.10(4.17)	16.64(16.71)
$[Er(D_2)_3]$	11.12	59	63.64(63.94)	4.20(4.38)	17.50(17.55)

In order to establish the binding mode of the azoderivate and Schiff bases to Er(III) in the complexes, FTIR spectrum of the free ligand was compared with the spectra of the metal complexes.[8]

o, o`- Dihydroxyazobenzene (DAB) (figure 1.) shows its characteristic bands in the 3055, 1572, 1469, 1349, 1257i cm^{-1} regions, assignable to νOH chelatic, νN=N, νC=C aromatic ring, νC_{arom}─ N, ν OH fenolic vibrations respectively.

In the complex the more affected bands are νN=N that is splited and become 1572sh cm^{-1}, and νOH fenolic that is shifted to 1240m cm^{-1} after complexation. The band νOH chelatic at 3055 $cm^{-1}$is unaffected in the complex and the bands correspond to coordinated water molecules are absent. These results showed that the ligand binds the metal by azo group and by one OH group that is shifted to 1240m cm^{-1} after complexation the other give the unaffected band at 3055 cm^{-1}.

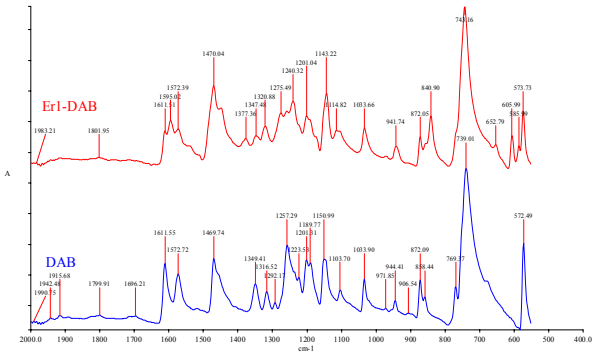


Fig. 1. FTIR spectra of the ligand (DAB) and the complex $[Er(DAB)_3]$.

o, - hydroxi - o` - carboxy azomethin (D_3) (figure 2.) the band assigned to νCH=N, 1618 cm^{-1} medium is splitted

and become more intense in the complex. In the complex the more affected band is νOH $_{fenolic}$ that is shifted from 1237i cm^{-1} in the ligand to 1257m cm^{-1} in the complex. The band νOH chelatic at 3026 cm^{-1}is slightly affected in the complex and appears at 3058 cm^{-1} and the bands correspond to coordinated water molecules are absent. These results showed that the ligand binds the metal by nitrogen of azomethin group and by one OH group that is shifted to 1257m cm^{-1} after complexation.

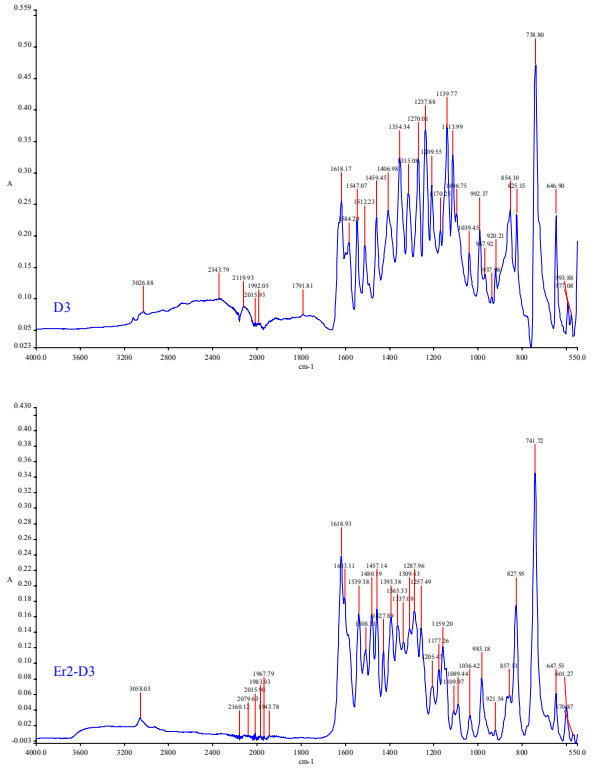


Fig. 2. FTIR spectra of the ligand D_3 and of the complex $[Er(D_3)_3]$.

o, o` - dihydroxi azomethin (D_2) (figure 3.) the band assigned to νC=O (COOH) in the ligand , disappears in the complex and it is replaced by a very intense band at 1585vi cm^{-1} corresponding to ν^{asim}C=O (COO$^-$) in the complex. The band νCH=N 1611i cm^{-1} in the free ligand is shifted as shoulder at 1601m cm^{-1}. The band νOH $_{fenolic}$ at 1272m cm^{-1}in the ligand is slightly affected in the complex and appears at 1268m cm^{-1}.The bands correspond to coordinated water molecules are absent. These results showed that the ligand binds the metal by nitrogen of azomethin group and by the oxygen atom of COOH group.

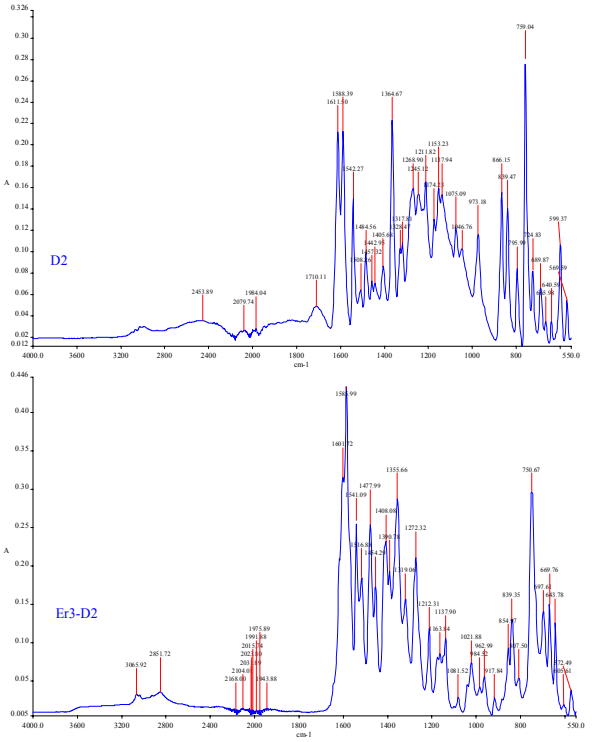


Fig. 3. FTIR spectra of the ligand D_2 and of the complex $[Er(D_2)_3]$.

The fluorescent properties were investigated for all complexes. We studied the influence of the N=N and C=N moieties on the fluorescent behaviour. In the table 2 are showed the maximum wavelengths of the excitation and the emission phenomena.

Table 2. The excitation, emission wavelengths of the Er(III) complexes.

Coordinative compounds	λ^{max}_{ex} (nm)	λ^{max}_{em} (nm)
I. $[Er(DAB)_3]$	300	400
II. $[Er(D_3)_3]$	380	450
III. $[Er(D_2)_3]$	380	450

The emission spectra of the Er(III) complexes are presented in the Figs. 4, 5, 6.

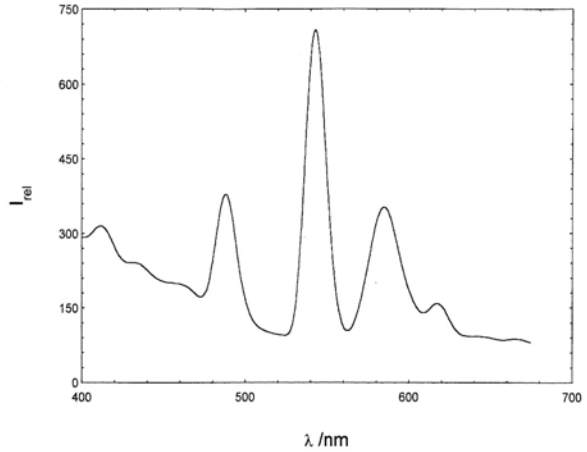


Fig. 4. The emission spectra of [Er(DAB)$_3$]

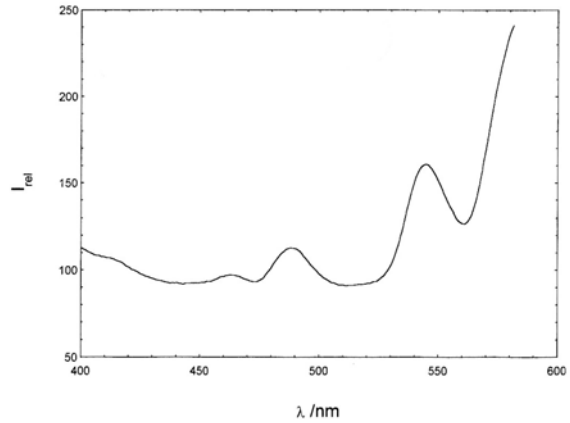


Fig 5. The emission spectra of [Er(D$_3$)$_3$].

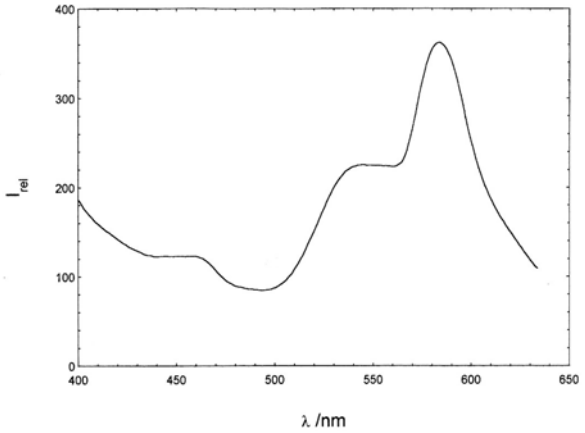


Fig. 6. The emission spectra of [Er(D$_2$)$_3$].

The emission spectrum of the [Er(DAB)$_3$] complex is more relevant than the other two complexes. The emission bands table 3. of the [Er(DAB)$_3$] complex were assigned according to the energetical levels of the Er^{3+} cation figure7.[9]

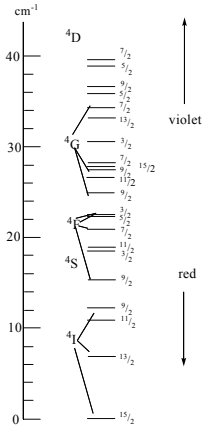


Fig. 7 . Energetical Levels of Er^{3+} cation

Table 3. The assigning of the emission bands of the [Er(DAB)$_3$] according to f-f transition of Er^{3+}

Coordination comp.	λ^{max}_{ex} (nm)	Emission λ (nm) and ^nT_i--- ^nT_i transition (j=1,2,3,4,5,6)			
		$^4I_{15/2}\rightarrow {}^4F_{3/2}$	$I_{15/2}\rightarrow {}^4S_{3/2}$	$^4I_{15/2}\rightarrow {}^4F_{9/2}$	$^4I_{15/2}\rightarrow {}^4F_{9/2}$
Er(DAB)$_3$]	300	440	540	590	620

All ligands used in reaction with Er(III) are dibasic and tridentate with the same potential donor groups of atoms (ONO) but they behave only as bidentate ligands with the donor group (ON). Probably the second oxygen is sterically hindered in the coordination bond. Although, there are not essential structural differences among the ligands the emission spectra of the complexes are very different. This behavior surely depend on the fluorescent property of the ligands. Dihydroxyazobenzene (DAB) is more fluorescent than o - hydroxi - o` - carboxy azomethin ( $D_3$ ) and o, o` - dihydroxi azomethin (D_2). Because of the only difference between (D_3) and (D_2) is the presence of COOH in D_3 and OH in D_2 and their fluorescent properties are comparable and less than (DAB), we suppose that the main factor that contributes directly on the increasing of the fluorescent properties of Er(III) complexes is the N=N azo group. We attributed this behaviour to the presence of the two lone pairs of the nitrogen atoms that positively contribute to the π conjugation in the chelatic rings comparable with the CH=N group that breaks the π conjugation in the chelatic rings.

4. Conclusion

In this paper coordination chemistry of an azoderivate and a Schiff bases ligands are described. All ligands are potentially tridentate and dibasic but they coordinate as bidentate and monobasic in a ratio metal to ligand 1/3. All the complexes are 6-coordinated and without coordinated water. The fluorescent properties of Er(III) complexes are increased by the azo group as a result of the extension of the π conjugation.

Acknowledgements

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*Corresponding author: emandi1988@ARtelecom.net