

Synthesis and Characterization of Six Novel Samarium (III) Complexes with L-aspartic Acid, L-glutamic Acid, Glycine and O-phenanthroline, Bipiridile as Ligands

Cardozo E.*; Contreras RR.*; Bellandi F.*; Lopez-Rivera A.**; Avendaño J.*; Araque C.*; Vielma J.*

Universidad de Los Andes, Facultad de Ciencias, *Laboratorio de Organometálicos.

**Laboratorio de Física Aplicada.

Núcleo Pedro Rincón Gutiérrez, La Hechicera, Mérida -5101 - Venezuela

e-mail: ecardozo@ula.ve; ricardo@ula.ve

Resumen: Se sintetizaron dos series diferentes de complejos de samario (III): Sm(o-Phen) (Lⁿ)₃ y Sm(bipy) (Lⁿ)₃ (n = 1-3; L¹ = ácido l-aspártico, L² = ácido l-glutámico, L³ = glicina) mediante métodos clásicos. Se utilizó una relación molar 3:1 de los ligandos Lⁿ, de o-fenantrolina o de biperidilo en cada caso. Los espectros UV-Vis muestran bandas agudas cerca de los 190 nm que corresponden al enlace Sm-O de alta energía así como transiciones f→f. Los espectros FT-IR confirman enlaces Sm-O en las señales situadas entre 490 - 450 cm⁻¹. Los análisis de TGA-DTA, EA y MS revelan una buena correlación con la propuesta estructural. Los cálculos computacionales utilizando métodos semiempíricos facilitan algunas propiedades que sirven de guía para el desarrollo de aplicaciones fotoluminiscentes y antibacteriales.

Palabras clave: Complejos de samario, tierras raras, aminoácidos, o-fenantrolina, biperidilo, cálculo computacional.

Abstract: Two different series of samarium (III) complexes, Sm (o-Phen) (Lⁿ)₃ and Sm (bipy) (Lⁿ)₃ (n = 1-3; L¹ = L-aspartic acid, L² = L-glutamic acid, L³ = glycine), were synthesized by classic methods. Ligands Lⁿ and o-phenanthroline or biperidile were used on a molar ratio 3:1 for each compound. UV-Vis reveals sharp signals near 190 nm corresponding to a high energy bond Sm-O and f→f transitions. FT-IR spectra shows itself a band between 490 - 450 cm⁻¹ indicative of Sm-O bond. Analytical analysis of TGA-DTA, EA and MS, resolve structural proposals. Computational calculation using semiempirical methods, show properties as a guide to approach better applications for these compounds like photoluminescence devices and antibacterial drugs.

Keywords: Samarium complexes, rare earth, amino acid, o-phenanthroline, biperidile, computational calculations.

1. INTRODUCTION

The number of studies which implies rare earth complexes have rapidly increased on last ten years because a wide capabilities of these metals as a photon receptors *via* antenna effects. High coordination numbers favor binding and catalyst functions. Ligands as o-phenanthroline and biperidile provide antenna effect [1-3] and L-aspartic, L-glutamic acids are natural proved chromophores [4-6]. In this paper, alternative synthesis method is used in order to reduce environmental impact caused by traditional ones used for this purposes. Characterization was carried out using UV-Vis, FT-IR, TGA-DTA, EA, MS and computational calculations using sparkle method [7, 8].

2. MATERIALS AND METHODS

2.1. Materials

All samarium complexes were prepared from samarium acetate monohydrate (SIGMA-ALDRICH). All reagents were analytical grade, and used without further purification.

2.2. Measurement of properties of samarium complexes

UV/Vis spectra were recorded on a Shimadzu Mini 1240 UV/Vis Spectrophotometer on 1 x 10⁻⁴ M solutions. FT-IR spectra were measured with a PE Spectrum RX1 on KBr pellets 5 % w/w. MS data were obtained from a HP GCMS 5988A. TGA/DTA measurements were recorded on TA INSTRUMENTS SDT-Q600. EA were obtained from a Thermo Scientific Fison EA-1108 CHNS-O. Computational calculations were carried out using MOPAC2009 as interface for AM1, PM3 and PM6 semi-empirical methods.

GABEDIT and AVOGADRO were also used for molecular modeling and visualization.

2.3. Preparation of samarium complexes

Accurately weighted each amino acid (L-aspartic, L-glutamic, glycine) with *o*-phenantroline on different reaction mixtures on 3:1 molar ratio for the Sm(*o*-phen)(Lⁿ)₃ series.

Same way for Sm(*bipy*)(L¹)₃ but weighting and mixing amino acids with bipyridile. A 70 % ethanolic solution (30 mL) was used as solvent heated to 74 °C (reflux temperature) [9, 10]. Samarium acetate was added to the mixture and stirred for 24 hours. Resulting solution was vacuum evaporated. Solid was washed three times with acetone (5 mL), dried and stored on dark glassware without light exposure.

3. RESULTS AND DISCUSSION

3.1. UV/vis spectra

The shape and intensity of the peaks on the complexes mainly depends of the ligands [11]. Characteristic absorption of *o*-phenantroline is 201, 227 and 267 nm; bipyridyl is 202, 233, 283 nm. The spectra show some blue shift indicating coordination of two nitrogens with the metal ion and a decrement of the conjugacy of benzene.

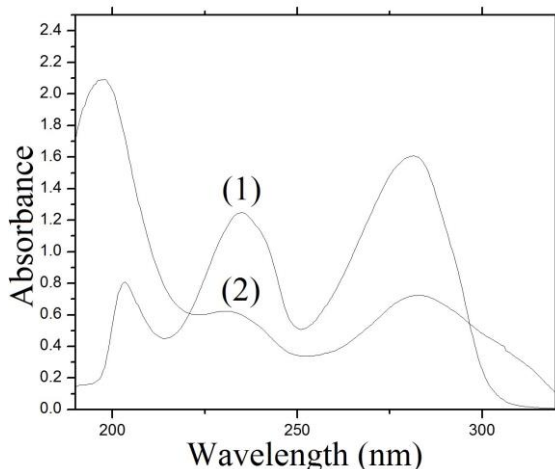


Figure 1. UV/Vis spectra of two series of samarium (II) complexes: (1) Sm(*o*-phen)(L¹)₃ series and (2) Sm(*bipy*)(L¹)₃ series. L¹ = aspartic acid; L² = glutamic acid and L³ = glycine; *o*-phen = *o*-phenantroline; *bipy* = bipyridyl.

3.2. FT-IR spectra

Table 1 and 2 shows the IR spectra for which ternary compound. Two bands between 1600 - 1700 cm⁻¹ and 1450 - 1550 cm⁻¹ can be attributed to symmetric and asymmetric vibrations of COO⁻ indicating coordination with the rare

earth ion. Besides, $\nu_{as} - \nu_s$, on complexes are lower than this difference on the free ligand showing that carboxylate have a bidentate chelating coordination.

Characteristic absorption band of -NH₃⁺ appears both, complex and ligands around the 3000 cm⁻¹ suggesting that the coordination do not proceed this way [12].

Table 1. Resume of most important FT-IR signals of ligands: L¹ = aspartic acid; L² = glutamic acid and L³ = glycine *o*-phen = *o*-phenantroline; *bipy* = bipyridyl.

Vibration Type	Ligands				
	L ¹	L ¹	L ¹	<i>o</i> -phen	<i>bipy</i>
νNH_3^+	3026 m	2966 m	2898 m	-	-
νCOOH	1690 s	1700 s	-	-	-
$\nu_{as}\text{COO}^-$	1608 s	1644 s	1612 s	-	-
$\nu_s\text{COO}^-$	1420 s	1422 s	1412 s	-	-
$\nu\text{C}=\text{C}$	-	-	-	1504 s	-
$\nu\text{C}=\text{N}$	-	-	-	1420 s	-
$\nu\text{C}=\text{C}$	-	-	-	-	1580 s
$\nu\text{C}=\text{N}$	-	-	-	-	1454 s
$\nu\text{O-H}$	-	-	-	3330 - 3422 s,b	3320 - 3428 s,b

Table 2. Resume of most important FT-IR signals of samarium (III) complexes: Sm(*o*-phen)(Lⁿ)₃ series and Sm(*bipy*)(L¹)₃ series.

Vibration Type	Samarium (III) complexes					
	Sm (<i>o</i> -phen) (L ¹) ₃	Sm (<i>o</i> -phen) (L ²) ₃	Sm (<i>o</i> -phen) (L ³) ₃	Sm (<i>bipy</i>) (L ¹) ₃	Sm (<i>bipy</i>) (L ²) ₃	Sm (<i>bipy</i>) (L ³) ₃
νNH_3^+	3018 m	3078 m	2915 m	3006 m	3077 m	2975 m
νCOOH	1692 s	1704 s	-	1697 s	1700 s	-
$\nu_{as}\text{COO}^-$	1592 s	1618 s	1596 s	1614 s	1588 s	1618 s
$\nu_s\text{COO}^-$	1416m,b	1417 m,b	1434 m	1488 m	-	1438 m
$\nu\text{C}=\text{C}$	1502 m	1509 m	1518 m	-	-	-
$\nu\text{C}=\text{N}$	1416m,b	1417 m,b	1416 m	-	-	-
$\nu\text{C}=\text{C}$	-	-	-	1572 w	-	1536 m
$\nu\text{C}=\text{N}$	-	-	-	1412 m	1412 m	1452 s
$\nu\text{O-H}$	3337 - 3390 s, b	3338 - 3388 m, b	3116 - 3378 s, b	3328 - 3390 s,b	3340 - 3400 s,b	3354 - 3413 s,b
$\nu\text{Sm-O}$	480 w	500 w	470 w	480 w	472 w	482 w

3.3. Mass spectrometry

Taking into account preliminary structures of complexes and obtained mass spectra, there is a good compliant with the initial structural proposals due to a molecular ion (P⁺) observed and fragments due to loss of ligands or part of them. This can lead to propose a fragmentation pattern for each structure.

Peaks observed on spectra will vary in a range between ± 1 *uma* and ± 6 *uma* due to action of different isotope distributions on ligands ¹³C (1.1122 %), ¹⁴⁴Sm (11.6540 %); ¹⁴⁷Sm (56.7670 %); ¹⁴⁸Sm (42.4810 %); ¹⁴⁹Sm (52.2560 %); ¹⁵⁰Sm (27.8200 %); ¹⁵²Sm (100 %); ¹⁵⁴Sm (84.9620 %)).

Table 2 and 3 resumes fragment losses and Fig. 2 show a fragmentation pattern.

Table 3. Main peaks (uma) observed for complexes Sm (o-phen)(Lⁿ)₃. L¹ = aspartic acid; L² = glutamic acid and L³ = glycine; o-phen = o-phenanthroline.

Sm (o-phen)(L ¹) ₃		Sm (o-phen)(L ²) ₃		Sm (o-phen)(L ³) ₃	
P ⁺	907.05	P ⁺	949.85	P ⁺	732.90
P ⁺ -(Asp)	774.60	P ⁺ -2(Glu)	802.30	P ⁺ -2(Gly)	656.85
P ⁺ -2(Asp)	641.35	P ⁺ -3(Glu)	654.95	P ⁺ -2(Gly)	582.20
P ⁺ -3(Asp)	508.20	P ⁺ -3(Glu)	508.15	P ⁺ -3(Gly)	507.50
P ⁺ -3(OAc)	730.20	P ⁺ -3(OAc)	772.20	P ⁺ -3(OAc)	555.10
P ⁺ -(o-phen)	727.96	P ⁺ -(o-phen)	769.95	P ⁺ -(o-phen)	552.55

Table 4. Main peaks (uma) observed for complexes Sm(bipy)(Lⁿ)₃. L¹ = aspartic acid; L² = glutamic acid and L³ = glycine; bipy = bipyridyl.

Sm (bipy)(L ¹) ₃		Sm (bipy)(L ²) ₃		Sm (bipy)(L ³) ₃	
P ⁺	882.95	P ⁺	925.25	P ⁺	708.55
P ⁺ -(Asp)	749.20	P ⁺ -2(Glu)	778.50	P ⁺ -2(Gly)	633.20
P ⁺ -2(Asp)	616.20	P ⁺ -3(Glu)	632.85	P ⁺ -2(Gly)	556.90
P ⁺ -3(Asp)	483.65	P ⁺ -3(Glu)	485.15	P ⁺ -3(Gly)	482.85
P ⁺ -3(OAc)	705.40	P ⁺ -3(OAc)	748.10	P ⁺ -3(OAc)	530.60
P ⁺ -(bipy)	725.90	P ⁺ -(bipy)	769.45	P ⁺ -(bipy)	551.95

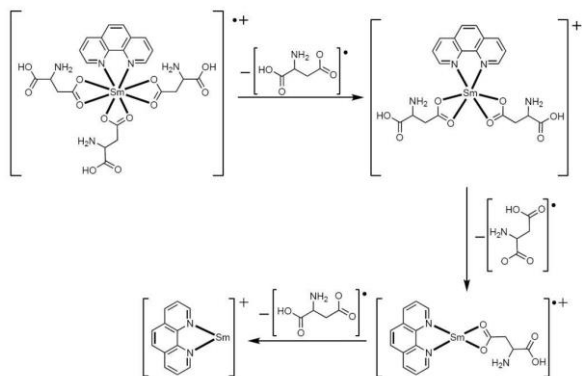


Figure 2. Fragmentation pattern for Sm (o-phen)(L¹)₃ complex. (L¹ = aspartic acid)

3.4. TGA-DTA analysis

The weightlessness of these compounds exhibited a good agreement with the stoichiometry. o-Phenanthroline losses its crystal water under the 100 °C. There are two main steps when complexes being heated. First one correspond to loss of cristal water on the complexes accompanied by an endothermic effect. The second refers to a decomposition of the anhydrous complexes to oxides accompanied by an exothermic effect with one, (or) two peaks.

Table 5. Loss of mass on the compounds and water of hidration. L¹ = aspartic acid; L² = glutamic acid and L³ = glycine; o-phen = o-phenanthroline; bipy = bipyridyl.

Complex	% W	T (°C)	Fragment	% W remaining
Sm(o-phen)(L ¹) ₃	8.573	123.42	4 H ₂ O	38.654
	52.773	234.35	Organic	
Sm(o-phen)(L ²) ₃	8.735	109.28	5 H ₂ O	31.179
	60.086	185.58	Organic	
Sm(o-phen)(L ³) ₃	2.096	60.59	1 H ₂ O	40.014
	57.890	201.27	Organic	
Sm(bipy)(L ¹) ₃	9.143	125.87	5 H ₂ O	41.447
	49.410	230.01	Organic	
Sm(bipy)(L ²) ₃	11.020	105.20	6 H ₂ O	32.261
	56.719	188.29	Organic	
Sm(bipy)(L ³) ₃	10.660	85.94	4 H ₂ O	36.029
	53.311	156.26	Organic	

3.5 Elemental analysis

Carbon, hydrogen and nitrogen analysis exhibit a good agreement with initial stoichiometry and all other analysis specially with TGA-DTA in which it is possible to establish exactly the same quantity of hydration water on each molecule:

Sm (o-phen) (L¹)₃ .4H₂O (Calc. SmC₃₀H₃₈N₅O₁₈: %C, 36.801 %H, 4.706; %N, 7.15): Found. %C, 36.931; %H, 4.966; %N = 7.879.

Sm (o-phen) (L²)₃.5H₂O (Calc. SmC₃₃H₄₄N₅O₁₈: %C, 41.723; %H = 5.195; %N, 6.744 %): Found. %C, 41.911; %H, 5.425; %N, 6.948.

Sm (o-phen) (L³)₃.H₂O (Calc. SmC₂₄H₃₂N₅O₁₂: %C, 35.780; %H, 4.973; %N, 8.705): Found. %C, 36.005; %H, 5.333; %N, 9.139.

Sm (bipy) (L¹)₃.5H₂O (Calc. SmC₂₈H₃₈N₅O₁₈: %C, 34.530; %H, 4.945; %N, 7.190): Found. %C, 34.775; H = 5.246 %; N = 7.503.

Sm (bipy) (L²)₃.6H₂O (Calc. SmC₃₁H₄₄N₅O₁₈: %C, 36.005; %H, 5.424; %N, 6.777): Found. %C, 36.402; %H, 5.686; %N, 6.913.

3.6. Computational calculations.

The Table 6 shows the methods used for all calculations, and results are showed on Table 7.

Most relevant result shown on this Table 7 is the COSMO volume, this can give a clear idea for select the most affordable complex to have further use as antibacterial agent. This selection represents a molecule with large surface that can be surrounded by many molecules of solvent like water. Sm (o-phen)(L²)₃ and Sm(bipy)(L²)₃ has higher volumes.

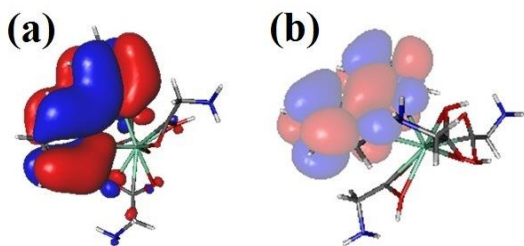
Table 6. Methods used for calculations of samarium (III) complexes. L¹ = aspartic acid; L² = glutamic acid and L³ = glycine; *o-phen* = o-phenantroline; *bipy* = bipyridyl.

Complex/method	AM1	PM3	PM6
Sm(<i>o-phen</i>)(L ¹) ₃	-	+	+
Sm(<i>o-phen</i>)(L ²) ₃	+	-	+
Sm(<i>o-phen</i>)(L ³) ₃	+	+	+
Sm(<i>bipy</i>)(L ¹) ₃	+	+	-
Sm(<i>bipy</i>)(L ²) ₃	+	-	+
Sm(<i>bipy</i>)(L ³) ₃	-	-	+

Table 7. Results of computational calculations for samarium (III) complexes. COSMO* = Solvation model: COnductor-likeScreeningMOdel. L¹ = aspartic acid; L² = glutamic acid and L³ = glycine; *o-phen* = o-phenantroline; *bipy* = bipyridyl.

Complex	Method	ΔH _f (kJ)	E _i (eV)	COSMO* area (Å ²)	COSMO* volumen (Å ³)
Sm(<i>o-phen</i>)(L ¹) ₃	PM3	-2184.43	7.68	530.08	700.47
	PM6	-2215.99	9.00	497.01	686.08
Sm(<i>o-phen</i>)(L ²) ₃	AM1	-2434.41	7.59	581.04	757.83
	PM6	-2237.91	8.64	548.52	749.51
Sm(<i>o-phen</i>)(L ³) ₃	AM1	-1206.09	8.70	382.43	495.99
	PM3	-1064.27	6.81	403.75	507.07
	PM6	-978.29	6.75	400.32	499.00
Sm(<i>bipy</i>)(L ¹) ₃	AM1	-2655.46	9.19	517.26	681.94
	PM3	-2430.72	9.30	536.89	686.08
Sm(<i>bipy</i>)(L ²) ₃	AM1	-2460.02	6.77	556.72	727.14
	PM6	-2234.28	7.38	532.41	728.77
Sm(<i>bipy</i>)(L ³) ₃	PM6	-1017.92	8.55	371.74	468.48

Analyzing the HOMO-LUMO surface for each complex (see Fig. 3), it is clearly that only one complex possibly have a good quantum yield because its HOMO and LUMO surface distribution around the molecule. Both surfaces are over the chromophore ligand on Sm(*bipy*)(L³)₃.

**Figure 3.** (a) HOMO surface and (b) LUMO surface for Sm(*bipy*)(L³)₃ complexes.

3.7. Catalytic trials

Proved catalytic activity of samarium (III) salts and complexes [13 – 15] leads to make some trials as follow.

All six complexes were tested with 1-hexene as substrate in presence of hydrogen for hydrogenation reactions. The conditions for all trials were: substrate catalyst ratio 100/1, 150 °C, 1000 psi and 24 h, a biphasic medium aqueous/ciclohexane was used. All complexes shows hydrogenation and isomerization capabilities. Results are shown on the Table 8.

Table 8. Results for catalytic trials. Conditions: substrate catalyst ratio 100/1, 150 °C, 1000 psi and 24 h, a biphasic medium aqueous/ciclohexane.

Complex	Percent (%)			
	1-Hexene	Hexane	cis-2-hexene	trans-2-hexene
Sm(<i>o-phen</i>)(L ¹) ₃	70.73	15.23	8.66	5.38
Sm(<i>o-phen</i>)(L ²) ₃	92.62	3.77	2.49	1.05
Sm(<i>o-phen</i>)(L ³) ₃	83.40	8.69	5.02	2.89
Sm(<i>bipy</i>)(L ¹) ₃	96.78	2.50	0.53	0.20
Sm(<i>bipy</i>)(L ²) ₃	69.05	15.62	9.17	6.15
Sm(<i>bipy</i>)(L ³) ₃	95.75	2.68	1.06	0.52

4. CONCLUSION

All six complex were successfully synthesized with a classic method that represent a low cost and low environmental impact synthesis. UV, IR, MS, EA and TGA-DTA technics reveals good accuracy with initial stoichiometry planned showing an effective bonding between O and N donors and RE(III) metal ion. Two complex possibly have better behavior as antibacterial agents: Sm(Glu)₃Phen, Sm(Glu)₃Bipy.

Sm(Gly)₃Bipy could have some photoluminiscent activity because a close distance between HOMO-LUMO surface on the chromophore ligand.

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