www.saber.ula.ve/avancesenquimica
Avances en Química, 10(Especial), 21-24 (2015)
Artículo científico

Synthesis, characterization and hydrogenation catalysis in biphasic medium (organic/water) of samarium (III) complex with glycine and 2,2-bipyridine ligands

Eduardo Cardozo*, **Joel E. Vielma, Bernardo Fontal, Ricardo R. Contreras, Marisela Reyes, Fernando Bellandi, Yuraima Fonseca, Victoria Romero.**

Laboratorio de Organometálicos. Departamento de Química. Facultad de Ciencias.
Universidad de Los Andes. Mérida 5101, Venezuela

(*) ecardozo@ula.ve

Recibido: 22/06/2015 **Revisado**: 25/08/2015 **Aceptado**: 01/09/2015
https://doi.org/10.53766/AVANQUIM/2015.10.01

Abstract

Sm(*bipy*)(*glycine*)$_3$ [bipy = 2,2-bipyridine] was synthesized by classic, microwave and mechanical methods. UV-Vis reveals a strong signal near 190 nm corresponding to a high energy Sm-O bond and $f \rightarrow f$ transitions. FT-IR spectra show a band between 490 - 450 cm^{-1} indicative of a Sm-O bond. TGA-DTA and MS analytical analysis, confirm the structural proposals. The samarium (III) complex was tested in 1-hexene hydrogenation, in biphasic media (cyclohexane/water) and the reaction parameters were optimized (time, temperature, substrate/catalyst ratio and H_2 pressure). Catalyst showed 37.5 % conversion.

Keywords: Catalysis; Hydrogenation; Samarium complex; Rare earth.

Resumen

El complejo Sm(*bipy*)(*glycine*)$_3$ [bipy = 2,2-bipiridina] fue sintetizado por tres métodos diferentes: clásico, microondas y mecano-química. El espectro UV-visible muestra una señal fuerte cerca de 190 nm que corresponde al enlace de alta energía Sm-O y a transiciones $f \rightarrow f$. En el espectro IR-TF se aprecia una banda entre 490 y 450 cm^{-1} que confirma la presencia del enlace Sm-O. Los análisis termo-gravimétricos TGA-DTA y la espectrometría de masas confirman la estequiometria inicial propuesta. El complejo de samario(III) fue estudiado en reacciones de hidrogenación de 1-hexeno en medio bifásico (ciclohexano/agua) y los parámetros de reacción (tiempo, temperatura, relación sustrato catalizador y presión de H_2) fueron optimizados. Se observó un 37,5 % de conversión.

Palabras clave: catálisis; hidrogenación; complejos de samario; tierras raras.

Introduction

The number of studies with rare earth complexes has increased rapidly on the last ten years, due to their wide capabilities as photon receptors *via* antenna effects[1]. On the other hand, lanthanides complexes have shown catalytic activity in olefin hydrogenation[2], moreover they can be used in asymmetric catalysis with high selectivity[3].

Today, microwave synthesis is widely studied and it is consistent with green chemistry principles[4]. In this paper, alternative synthesis methods are used in order to reduce environmental impact caused by traditional methods. Sm(*bipy*)(*glycine*)$_3$ was characterized using UV-Vis, FT-IR, TGA-DTA, MS and studied in a hydrogenation reaction using a biphasic system (cyclohexane/water).

Materials and methods

Materials

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

Measurement of samarium complex properties and catalytic studies

UV/Vis spectra were recorded on a *Shimadzu Mini 1240 UV/Vis Spectrophotometer* on 1x10^{-4} M aqueous 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 acquired using a *TA INSTRUMENTS SDT–Q600*. Catalytic trial analysis was recorded on a *Perkin-Elmer Autosystem 900 GC* with an methyl silicone capillary column *Quadrex* (50 m long and 0.52 µm diameter).

Preparation of samarium (III) complex Sm(*bipy*)(*glycine*)$_3$

Amino acid (glycine) and bipy were added on 3:1 molar ratio to 70 % ethanolic solution (30 mL) and heated to 74 °C (reflux temperature)[5]. Samarium acetate was added to the mixture and stirred for 24 hours. The resulting solution was vacuum evaporated. A solid precipitated was washed three times with acetone (5 mL), dried and stored in a dark glassware without light exposure. Reaction yield was 62.4 %.

Microwave synthesis was carried out mixing the same molar ratio and quantities described above on 10 mL of ethanol 99 %. Eight pulses of 15 seconds were applied on a PANASONIC Household Microwave @ 60 % of nominal power (1200 W) leaving a 5 seconds of relaxation time between pulses completing a total time of 160 seconds. The solid produced was washed three times with acetone (5 mL), dried and stored in dark glassware without light exposure. Reaction yield was 35.6 %.

Mechano-chemical synthesis consists in accurately mixing the molar ratio and adding drop-wise 5 mL of ethanol 99 %. After crushing the mixture for 30 minutes, the solid produced was washed three times with acetone (5 mL), dried and stored on dark glassware without light exposure. Reaction yield was 12.8 %.

Catalytic trials

The catalytic reactions were performed on 10 mL *Parr Instruments* batch reactors. The temperature was provided by vertical heating ovens and monitored by PID temperature controllers and type K thermocouples. The reactions were performed as follows: 2.5 mL of cyclohexane and 2.5 mL of water were added in the reactor jacket, then 0.0050 g of samarium (III) catalyst was added and 1-hexene substrate according to substrate/catalyst ratio required; The reactor was closed and charged with appropriate H_2 pressure, and the reactor was placed into the heating oven. Initial time starts just before the reaction reached the temperature set up on the controller.

Results and discussion

Synthetic methods

Sm(*bipy*)(*glycine*)$_3$ was prepared by three different methods (classical, microwave and mechano-chemical synthesis). Classical synthesis showed overall best reaction yield (62.4 %), however the time used by microwave synthesis (160 seconds) and the use of less quantity of solvent makes this synthesis method more promising in the development of green chemistry.

Uv/vis spectra

The shape and intensity of the peaks on the complexes mainly depends on the ligands[6]. Characteristic absorption of bipy in 202, 233, 283 nm can be appreciated in figure 1. The spectra show a blue shift evidencing coordination of two nitrogen atoms with the metal ion and a benzene conjugation decrease.

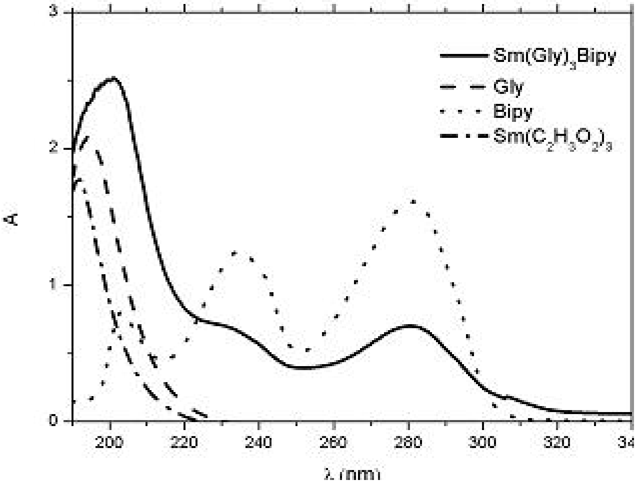

Fig. 1: UV/Vis spectra of Sm(*bipy*)(*glycine*)$_3$; Glycine; Bipyridine and Sm acetate

FT-IR spectra

Figure 2 shows the IR spectra of the non-coordinated glycine (a) and bipy (b) in which it is possible to observe the most important characteristic bands at 2898, 1612 and 1412 cm^{-1} corresponding to νNH_3, $\nu_{as}COO^-$ and $\nu_s COO^-$ respectively to glycine and $\nu C{=}C$ in 1580 cm^{-1} and $\nu C{=}N$ in 1454 cm^{-1} to bipy. In the figure 2(c), IR spectra of Sm(*bipy*)(*glycine*)$_3$ showed all characteristics bands of ligands glycine and bipy with a shift of the following bands: $\nu_{as}COO^-$, $\nu_s COO^-$ and $\nu C{=}N$ leading to guess an effective coordination of both ligands.

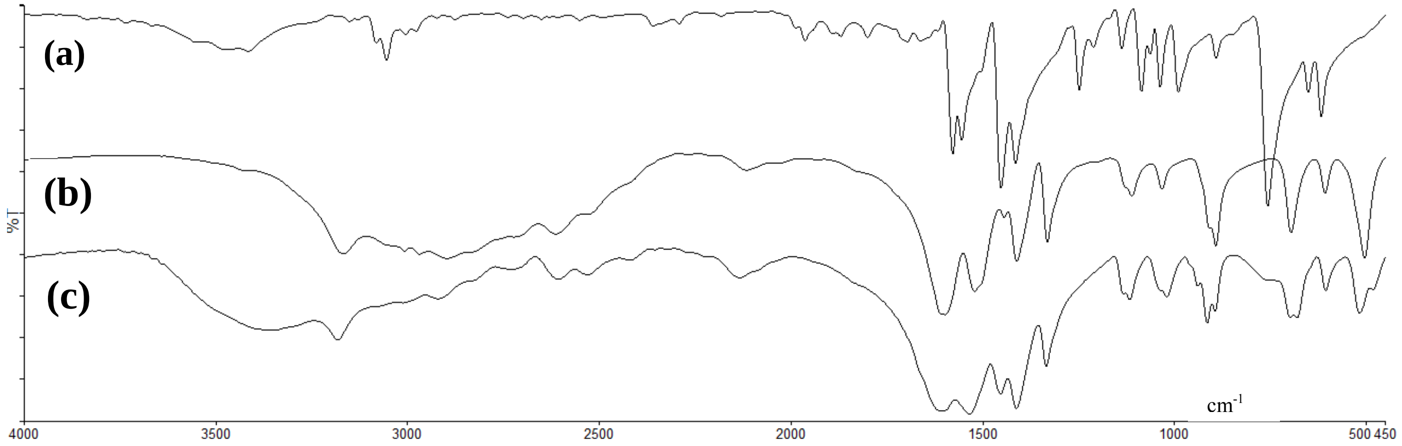

Fig. 2: IR spectra of bipy (a), glycine (b) and Sm(*bipy*)(*glycine*)$_3$ (c).

Mass spectrometry

Taking into account the preliminary structures of complexes and the obtained mass spectra, there is a good agreement with the initial structural proposals due to a molecular ion (P^+) observed and fragments due to loss of ligands. This allow the proposal of a fragmentation pattern for the structure of Sm(*bipy*)(*glycine*)$_3$. (see table 1 and figure 3 below).

Table 1: Main peaks (uma) observed for the complex Sm(*bipy*)(glycine)$_3$.

Sm(*bipy*)(glycine)$_3$	
P^+	708.55
P^+ -(glycine)	633.20
P^+ -2(glycine)	556.90
P^+ -3(glycine)	482.85
P^+ -3(OAc)	530.60
P^+ -(bipy)	551.95

Peaks observed on the MS spectra will vary in a range between ± 1 *uma* and ± 6 *uma* due to action of different isotope distributions/ relative abundance on ligands ^{13}C (1.11 %), ^{144}Sm (3.07 %); ^{147}Sm (14.99 %); ^{148}Sm (11.24 %); ^{149}Sm (13.82 %); ^{150}Sm (7.38 %); ^{152}Sm (26.75 %); ^{154}Sm (22.75 %). Table 2 indicates the fragment losses and figure 3 shows a fragmentation pattern.

Table 2: Mass loss and hydration water on the samarium (III) complex.

% W	T (°C)	Fragment	% W remaining
10.660	85.94	4 H_2O	36.029
53.311	156.26	Organic	

TGA-DTA analysis

The weight losses of these compounds exhibited a good agreement with the stoichiometry. There are two main steps when complexes being heated. The first one corresponds to crystal water loss on the complex accompanied by an endothermic process. The second one refers to a decomposition of the anhydrous complexes to oxides accompanied by an exothermic process with one, and two peaks.

Catalytic trials

Sm(*bipy*)(*glycine*)$_3$ was tested in hydrogenation reactions in a biphasic system (cyclohexane/water) using 1-hexene as substrate. The conditions of reactions were optimized exploring the reactions under the following conditions: time = from 12 to 72 h; temperature = from 125 to 225 °C; substrate/catalyst ratio = from 50:1 to 400:1 and H_2 pressure = from 400 to 1.200 psi. The optimal parameters were: time = 24 h, temperature = 175 °C, substrate/catalyst ratio = 100:1 and H_2 pressure = 1000 psi, under optimal conditions, a 37.5 % maximum conversion was obtained.

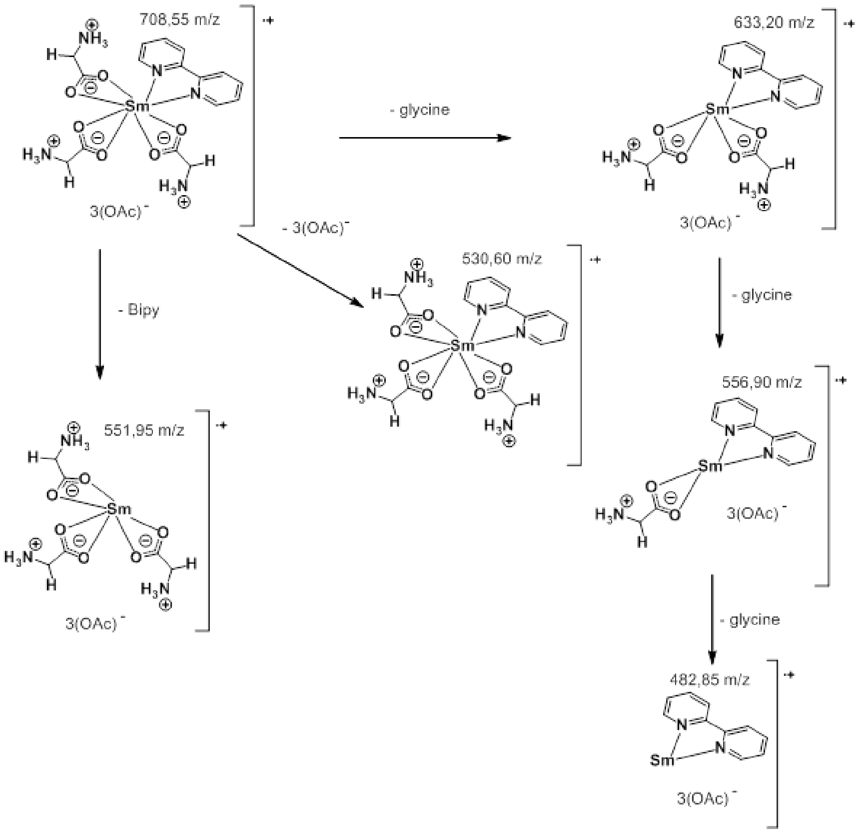

Fig. 3: Fragmentation pattern for Sm(bipy)(glycine)$_3$ complex.

Conclusion

Sm(*bipy*)(*glycine*)$_3$ was successfully synthetized with three different methods showing the microwave synthesis like a promising alternative for development of green chemistry due to low cost and low environmental impact. UV, IR, MS, and TGA-DTA technics reveals good agreement with ini-tial stoichiometry proposal, showing an effective bonding between O and N donors and Sm(III) metal ion. Under moderate conditions Sm(*bipy*)(*glycine*)$_3$ showed moderate activity in 1-hexene hydrogenation in a biphasic system (cyclohexane/water) with a maximum conversion of 37.5 %.

Acknowledgement

We thank CDCHTA-ULA (Proy C-1945-15-08-B) for financial support.

References

1. (a) L Liu, X Xu, Z Lou, F. Zhang, J Pei. Luminiscent properties of a novel terbium complex Tb(o-BBA)$_3$(Phen). **J. Rare Earths**. **21(1)**, 253–256 (2006).

   (b) R Kumar, U Singh. Molecular structure, photophysical and thermal properties of samarium(III) complexes. **J. Mol. Struct.**, **872,** 427–434 (2008).

   (c) L Armelao, S Quici, F Barigelletti, G Accorsi, G Bottaro, M Cavazzinib, E Tondello. Design of luminiscent lanthanide complexes: From molecules to highly efficient photoemitting materials. **Coord. Chem. Rev., 254,** 487–505 (2010).

   (d) P Gawryszewska, J Lisowski. Lanthanide(III) complexes of N$_4$O$_4$ Schiff base macrocycle: Luminescense and formation of hetero-dinuclear d-f complexes. **Inorg. Chim. Acta**, **383,** 220–229 (2012).

   (e) Z Ahmed, K Iftikhar. Synthesis, luminescence and NMR studies of lanthanide (III) complexes with hexafluoro-acetylacetone and phenanthroline. Part II. **Inorg. Chim. Acta**, **392,** 165–176 (2012).

   (f) Z Piskula, J Czajka, K Staninski, S Lis. Luminescense properties of calcium tungstate activated by lanthanide (III) ions. **J. Rare Earths, 32(3),** 221–225 (2014).

2. (a) GA Molander, J Winterfeld. Organolanthanide catalyzed hydrogenation and hydrosilylation of substituted methylene-cycloalkanes. **J. Organomet. Chem.**, **554**, 275-279 (1996).

   (b) G Jeske, H Lauke, H Mauermann, H Schumann, TJ Marks. Highly Reactive Organolanthanides. A Mechanistic Study of Catalytic Olefin Hydrogenation by Bis(pentamethylcyclo-pentadienyl) and Related 4f Complexes. **J. Am. Chem. Soc.,** **107**, 8111-8118 (1985).

   (c) WJ Evans, JH Meadows, WE Hunter, JL Atwood. Organolanthanide and Organoyttrium Hydride Chemistry. 5. Improved Synthesis of [(C$_5$H$_4$R)$_2$YH(THF)]$_2$ Complexes and Their Reactivity with Alkenes, Alkynes, 1,2-Propadiene, Nitriles, and Pyridine, Including Structural Characterization of an Alkylideneamido Product. **J. Am. Chem. Soc**., **106**, 1291-1300 (1984).

   (d) VP Conticello, L Brard, MA Giardello, Y Tsuji, M Sabat, CL Stern, TJ Marks. Chiral Organolanthanide Complexes for Enantioselective Olefm Hydrogenation. **J. Am. Chem. Soc**., **114**, 2761-2762 (1992).

3. MA Giardello, VP Conticello, L Brard, MN Gagné, TJ Marks. Chiral Organolanthanides Designed for Asymmetric Catalysis. A Kinetic and Mechanistic Study of Enantioselective Olefin Hydroamination/Cyclization and Hydrogenation by C 1-Symmetric Me$_2$Si(Me$_4$C$_5$)(C$_5$H$_3$R)Ln Complexes where R = Chiral Auxiliary. **J. Am. Chem. Soc**., **116**, 10241-10254 (1994).

4. (a) BL Hayes. Microwave Synthesis Chemistry at the Speed of Light. CEM Publishing, USA (2002).

   (b) CO Kappe, D Dallinger, SJ Murphree. Practical Microwave Synthesis for Organic Chemistry: Strategies, Instruments and Protocols. Wiley-VCH, Germany (2009).

5. (a) R Freire, N da Costa, G Rocha, AM Simas. Sparkle/AM1 Parameters for the modeling of samarium(III) and promethium (III) complexes. **J. Chemical Theory and Computation**, **2(1),** 64–74 (2006).

   (b) R Freire, N da Costa, G Rocha, AM Simas. Sparkle/PM3 Parameters for the modeling of samarium (III) and promethium (III) complexes. **J. Chemical Theory and Computation**, **3(1),** 1588–1596 (2007).

6. Y Hui, H Qizhuang, Y Jing, Z Wenjie. Syntheses, characterization and antibacterial properties of rare earths (Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Er^{3+}) complexes with L-aspartic acid and o-phenanthroline. **J. Rare Earths**, **24(1)**, 4-8 (2006).