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Covalent lanthanide (III) macrocyclic complexes: Bonding nature and optical properties of a promising single antenna molecule[†]

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The present work is focused on the elucidation of the electronic structure, bonding nature and optical properties in a series of low symmetry (C_2) coordination compounds of the type $[Ln^{III}HAM]^{3+}$, where “ Ln^{III} ” are the trivalent lanthanide ions: La^{3+} , Ce^{3+} , Eu^{3+} and Lu^{3+} , while “HAM” is the neutral six-nitrogen donor macrocyclic ligand $[C_{22}N_6H_{26}]$. This systematic study has been performed on the framework of the Relativistic Density Functional Theory (R-DFT) and also from a multi-reference approach via the Complete Active Space (CAS) wavefunction treatment with the aim to analyze their ground state and excited states electronic structure as well as electronic correlation. Furthermore, the use of the energy decomposition scheme proposed by Morokuma-Ziegler, and the electron localization function (ELF) allow us to characterize the bonding nature between the lanthanide ions and the macrocyclic ligand, obtaining as a result a dative-covalent interaction. Due to the great deal of the lanthanide optical properties and its technological applications, the absorption spectra of this set of coordination compounds were calculated using the time-dependent density functional theory (TD-DFT), where the presence of the intense Ligand to Metal Charge Transfer (LMCT) bands on the ultraviolet and visible region, and the inherent $f-f$ electronic transitions in the Near-Infrared (NIR) region for some lanthanide ions, allow us to propose these systems as “single antenna molecules” with potential applications in NIR technologies.

1 Introduction

It is not an overstatement that the study of metal macrocyclic complexes is a kind of “centre of life” topic, particularly due to its several applications. We can mention its important role on several biological human being processes as well as its technological applications in fields like biology, chemistry, biochemistry, physics and applied medicine.^{1–4} As we mentioned before, the research in metal macrocyclic complexes have had a significantly impact on many fields, this is from its earliest uses as a protein-metal binding sites model in biological metalloproteins systems, to our days when the use of lanthanides or actinides instead of transition metals introduce another valuable contribution of unique chemical properties from their inherent electronic structure, promoting plenty of the actual technological applications like: optics^{5–9}, optoelectronics (LED and OLED)¹⁰, magnetism (single molecule magnets), magnetic resonance imaging^{4,11}, luminescent probes¹², biomarkers¹³, etc.

This wide range of areas where metal macrocyclic complexes are involved made the coordination chemistry of these systems a fascinating area of active research in inorganic, bio-inorganic, materials science and also in theoretical chemistry.

Furthermore, the ability of lanthanide and actinide metal ions to promote Schiff base condensation of the appropriated diamine and dicarboxylic precursors, gave as a result the formation of stable metal complexes of otherwise inaccessible macrocyclic ligands, which served as a springboard to explore their coordination chemistry. A prove of this, are the research works developed by A. M. Arif¹⁴, L. De Cola^{15,16}, D. Fenton^{17–19}, G. Bombieri and L. M. Vallarino^{20–26}, in which a template synthetic route was used to achieved “2+2” 18-membered lanthanide hexa-aza macrocycle derived from pyridine head units and aliphatic lateral units with all lanthanide ($C_{22}N_6H_{26}$) series except for Promethium.² The molecular structure of these coordination compounds were determined by X-ray diffraction analysis and NMR (1H and ^{13}C) spectra; other characterization techniques related with the stability, like thermogravimetric measurements, showed that these compound are thermally stable in the solid state.

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One significant aspect of the lanthanides ions are their particular spectroscopic properties. Trivalent cations display poor absorption and emission bands that correspond to the low extinction coefficients of the Laporte forbidden $f \rightarrow f$ electronic transitions, making the direct excitation of the metals inefficient and useless. The use of strongly absorbing antenna chromophores is a strategy to stimulate luminescence of lanthanide elements conferring strongly emissive and long-lived excited states (antenna effect).^{27,28} Unfortunately, due to the time-demand and the complexity on modeling lanthanide (or actinide) macrocyclic compounds there are few studies reported, particularly in reference to the $[\text{Ln}^{\text{III}}[\text{C}_{22}\text{N}_6\text{H}_{26}]]^{3+}$ complexes.

In the present work we study the lanthanide hexa-aza macrocyclic complexes, in order to analyze deeply their electronic structure and elucidate the nature of the bonding interaction between the lanthanide center and the macrocyclic ligand. This research deals with the calculation of the ground and excited states and also the photophysical properties of this series of compounds in which the light is absorbed by π -chromophore, in our case the macrocyclic ring, is used as an antenna group to properly sensitize NIR luminescence of some lanthanide ions.

2 Computational Details

2.1 DFT Calculations

The calculations were performed considering the molecular structure presented in Figure 1, which is based on the experimental crystallographic data reported by Arif¹⁴, Vallarino and

co-workers.^{16,20–22} All of these lanthanide hexa-aza macrocyclic complexes are commonly called as $[\text{Ln}^{\text{III}}\text{HAM}]^{3+}$, where HAM is the neutral six-nitrogen macrocyclic ligand $\text{C}_{22}\text{N}_6\text{H}_{26}$, and Ln^{III} are trivalent lanthanide ions. We choose the following lanthanide ions: La^{3+} , Ce^{3+} , Eu^{3+} and Lu^{3+} , in order to describe the electronic structure of the lanthanide series and the interaction with the macrocyclic ligand when the f -shell of the lanthanide center is: empty, has only one electron, is almost half-filled (six electrons) and finally, when is full-filled.

All geometrical, electronic structures and optical properties were calculated using the Amsterdam Density Functional (ADF) package²⁹; these calculations were also performed at a relativistic level of theory in a spin-restricted and spin-unrestricted scheme for closed shell ($[\text{LaHAM}]^{3+}$, $[\text{LuHAM}]^{3+}$) and open shell ($[\text{CeHAM}]^{3+}$, $[\text{EuHAM}]^{3+}$) systems respectively. The scalar effects and the spin-orbit coupling (SOC) were incorporated by means of a two-component Hamiltonian with the zeroth-order regular approximation (ZORA).^{30,31} Furthermore, all the study was done considering a C_2 symmetry point group, where the inclusion of the spin and therefore the SOC effect, demands the use of the C_2^* double-valued group of symmetry, with the aim to make a better interpretation of the results.

The ground state of all molecular structures presented in this work were fully optimized at scalar relativistic level, via the analytical energy gradient method implemented by L. Verluis and T. Ziegler and using the generalized gradient approximation (GGA)³² with the exchange-correlation functional proposed by Perdew-Burke-Ernzerhof (PBE)³³, which was

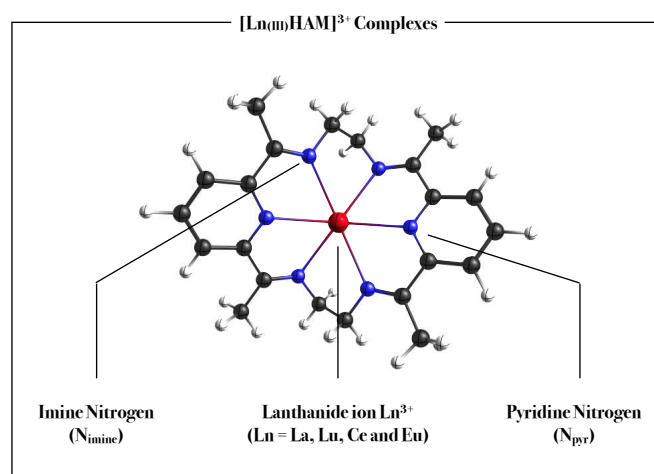


Fig. 1 Selected molecular structure for each lanthanide hexa-aza macrocyclic complexes

previously reported that work in good accuracy for lanthanide and actinide organometallic compounds. Additionally, the triple- ζ quality Slater-type orbital (STO) basis set with two polarization functions (TZ2P) were used for all atoms.³⁴

For all molecular systems, the geometry optimization of the first excited state were also carried out. We choose the first excited electronic configuration from the most common emissive states for the studied lanthanides. According to this and considering that over a C_2 symmetry, all electronic transition among any irreducible representations becomes allowed, this permit us to suggest that the lowest f -excited-state will be the emissive state. Therefore, for the non-luminescent [LaHAM]³⁺ and [LuHAM]³⁺ complexes we choose the first singlet excited-state (in order to have the same multiplicity). For the luminescent systems, [CeHAM]³⁺ and [EuHAM]³⁺, we choose the most common emissive states for the lanthanide ions, that means a doublet excited-state on the case of the cerium ($^2F_{5/2} - ^2F_{7/2}$), and a quintuplet with a spin-flip possibility for the europium complexes ($^7F_J - ^5D_J$). In all these cases, the gradients of the excitation energy and the ground state are combined to give the gradients of the excited state; these can be used in much the same way as the ground state gradients are used. Therefore, this allow us to study any distortion in geometrical parameters that could lead into a variation on the excitation energies and consequently a shift on the absorption-emission spectra, this shift is well-known in photochemistry as "Stokes shift". After all geometry optimizations, a frequency analysis was performed by using the analytical second derivatives method implemented in ADF code, where we obtained only positive frequencies for all [Ln^{III}HAM]³⁺ systems confirming they are minima on the potential energy surface.

In order to study the bonding nature in this lanthanide hexa-aza macrocyclic complexes, several schemes of study were used. Firstly, an analysis of bonding energetics were performed by combining a fragment approach to the molecular structure of a chemical system with the decomposition of the total bonding energy (E_{BE}), according to Morokuma-Ziegler energy partitioning scheme³⁵, as:

$$E_{BE} = E_{Pauli} + E_{Estat} + E_{Orb} \quad (1)$$

Where E_{Pauli} , E_{Estat} and E_{Orb} are, the Pauli repulsion, electrostatic interaction, and orbital-mixing terms, respectively. A detailed description of the physical significance of these properties has been given by Bickelhaupt and Baerends.³⁶ The electrostatic component is calculated from the superposition of the unperturbed fragment densities at the molecular geometry and corresponds to the classical electrostatic effects

associated with coulombic attraction and repulsion. The electrostatic contribution is most commonly dominated by the nucleus-electron attractions and therefore has a stabilizing influence. The Pauli component is obtained by requiring that the electronic antisymmetry conditions must be satisfied and has a destabilizing character, whereas the orbital-mixing component represents a stabilizing factor originating from the relaxation of the molecular system due to the mixing of occupied and unoccupied orbitals and can involve electron pair bonding, charge-transfer or donor-acceptor interactions, and polarization.

Afterwards, the electron localization function (ELF), which was developed by A. D. Becke and K. E. Edgecombe³⁷, was computed with the DGRID 4.6 program³⁸ using the first calculated densities for all [Ln^{III}HAM]³⁺ systems. The ELF is defined as follows:

$$ELF = \left[1 + \left(\frac{C(r)}{C_{h(r)}} \right)^2 \right]^{-1} \quad (2)$$

Where, $C(r)$ represents the excess of local kinetic energy density due to the Pauli exclusion principle and $C_{h(r)}$ is the Thomas-Fermi kinetic energy density, which can be regarded as a "renormalization" factor. The local maximum of the ELF, whose values are within the [0,1] interval, define localization attractors corresponding to the core, bonding and non-bonding electron pairs and their spatial arrangement.³⁹ The results of the ELF analysis were visualized with the MOLEKEL 5.4 software.⁴⁰ Moreover, net charge analysis of the metal center and charge transfer phenomena were evaluated using different populations analysis schemes like Mulliken^{41,42}, Hirschfield⁴³, Voronoi⁴⁴ and the natural bonding Orbital (NBO).⁴⁵

In order to calculate the absorption spectra of these molecules, the excitation energies were calculated using the time-dependent density functional theory (TD-DFT)⁴⁶ at scalar relativistic level for both closed and open shell systems; in addition, SOC was included on the calculation of the excitation energies only for closed shell molecules^{47,48}, since the algorithm for open shell systems has not been implemented. The excitation energies were calculated using the statistical average of orbital exchange-correlation model potential (SAOP)⁴⁹, which was specially designed for the response property calculations, particularly for spectroscopic properties, since the model potential has asymptotic corrections. On this part of the study, we have a special interest on electronic transitions lying in the near infrared (NIR) region, since these transitions have significant importance on biological, medical and optoelectronic applications.

2.2 Wave-function Calculations

Additionally to the DFT calculations and with the aim to describe properly the particular multi-configurational behaviour of the open shell lanthanide ions (Ce^{3+} and Eu^{3+} cases), the Complete Active Space Self Consistent Field (CASSCF)⁵⁰ approximation was used in order to obtain a good description on their electronic states for all the open shell molecules. All these calculations were done with the ORCA 3.0 suite of programs⁵¹, where the active space selected was one electron in seven orbitals CAS(1,7) and six electrons in seven orbitals CAS(6,7) for Ce^{3+} and Eu^{3+} respectively. The active space described above has proved to give good results for these kind of molecular systems. Dynamic correlation was calculated by using the N-Electron Valence Perturbation Theory (NEVPT2).^{52–54} The spin-orbit coupling (SOC) and spin-spin coupling (SSC) were calculated via a multi-reference type such as Multi-Reference Configuration Interaction (MRCI).^{55,56}

3 Results and Discussions

3.1 Structural and Molecular Orbital Analysis

The calculated ground state geometries for all $[\text{Ln}^{\text{III}}\text{HAM}]^{3+}$ complexes are in good agreement with the experimental X-ray diffraction data obtained by Arif¹⁴ and Vallarino et al.^{16,20–22} The results of geometry optimizations for the ground and the first excited-state are reported in Table 1, where we can observe that the bond lengths have a variation between 0.1–0.2 Å with respect to the experimental data giving an error of ~ 1 ; whilst for the angles and dihedral angles, the calculated results have a deviation among 4.0–6.0 degrees from the crystal structure, which lead an average error of ~ 5 . For all ground states is observed a continuous decrease on the $\text{Ln}-\text{N}_{(\text{pyr})}$ distance as follows: $[\text{LaHAM}]^{3+} > [\text{CeHAM}]^{3+} > [\text{EuHAM}]^{3+} > [\text{LuHAM}]^{3+}$ and also a steadily decrease on the dihedral angle of the di-imine bridge ($\angle \text{N}_{\text{imine}}-\text{C}-\text{C}-\text{N}_{\text{imine}}$) through the series.

Table 1 Experimental and calculated geometrical parameters. Bond lengths (Å), angles and dihedral angles (Deg) for the ground state and first excited-state on $[\text{Ln}^{\text{III}}\text{HAM}]^{3+}$ systems, under a C_2 symmetry point group.

Closed-Shell	$[\text{LaHAM}]^{3+}$			$[\text{LuHAM}]^{3+}$		
	Exp. ^a	Ground State	Excited State	Exp. ^b	Ground State	Excited State
d $\text{Ln}-\text{N}_{\text{pyr}}$	2.746 - 2.764	2.623	2.620	2.552 - 2.555	2.377	2.352
d $\text{Ln}-\text{N}_{\text{imine}}$	2.672 - 2.704	2.584	2.622	2.471 - 2.501	2.384	2.386
	2.727 - 2.729	2.630	2.625	2.581 - 2.608	2.463	2.435
$\angle \text{N}_{\text{pyr}}-\text{Ln}-\text{N}_{\text{pyr}}$	— [†]	173.4	170.6	— [†]	134.5	133.4
$\angle \text{N}_{\text{pyr}}-\text{Ln}-\text{N}_{\text{imine}}$	58.6 - 58.7	61.2	60.5	61.2-61.8	64.2	64.7
	59.0 - 59.2	61.5	61.0	61.6 - 61.9	66.2	66.7
$\angle \text{N}_{\text{imine}}-\text{Ln}-\text{N}_{\text{imine}}$	69.9 - 63.6	63.7	64.3	63.0 - 63.5	64.7	65.1
$\angle \text{N}_{\text{imine}}-\text{C}-\text{C}-\text{N}_{\text{imine}}$	— [†]	53.7	54.5	52.2 - 54.9	47.5	46.1
Open-Shell	$[\text{CeHAM}]^{3+}$			$[\text{EuHAM}]^{3+}$		
	Exp. ^a	Ground State	Excited State	Exp. ^c	Ground State	Excited State
d $\text{Ln}-\text{N}_{\text{pyr}}$	2.726 - 2.637	2.600	2.538	2.543 - 2.657	2.552	2.538
d $\text{Ln}-\text{N}_{\text{imine}}$	2.617 - 2.622	2.542	2.552	2.489 - 2.592	2.511	2.508
	2.719 - 2.617	2.579	2.557	2.539 - 2.669	2.584	2.579
$\angle \text{N}_{\text{pyr}}-\text{Ln}-\text{N}_{\text{pyr}}$	— [†]	146.2	146.9	— [†]	145.1	144.7
$\angle \text{N}_{\text{pyr}}-\text{Ln}-\text{N}_{\text{imine}}$	59.6 - 59.9	61.5	61.8	60.5 - 61.1	61.7	61.9
	59.9 - 60.3	61.9	62.2	61.3 - 61.7	62.5	62.8
$\angle \text{N}_{\text{imine}}-\text{Ln}-\text{N}_{\text{imine}}$	61.7 - 61.9	63.7	64.6	61.7 - 62.8	63.8	63.5
$\angle \text{N}_{\text{imine}}-\text{C}-\text{C}-\text{N}_{\text{imine}}$	— [†]	52.2	52.5	48.1 - 55.1	51.2	50.2

^a Ref¹⁴, ^b Ref²⁰, ^c Ref^{21,22}, [†] Not Available Experimental Data

Table 2 Experimental and calculated IR frequencies (cm^{-1}) and intensities ‡ (km/mol) for all $[\text{Ln}^{\text{III}}\text{HAM}]^{3+}$ at scalar relativistic level

	$[\text{LaHAM}]^{3+}$		$[\text{CeHAM}]^{3+}$		$[\text{EuHAM}]^{3+}$		$[\text{LuHAM}]^{3+}$	
	Exp. ^a	Calc.	Exp. ^a	Calc.	Exp. ^a	Calc.	Exp. ^a	Calc.
$\nu_{\text{C}=\text{N}_{\text{pyr}}}$	1652	1603 66b [†] 184.1 [‡]	1650	1584 63b [†] 107.9 [‡]	1655	1604 66b [†] 158.0 [‡]	1660	1597 66b [†] 223.5 [‡]
$\nu_{\text{C}=\text{N}_{\text{imine}}}$	1590	1571 64b [†] 156.9 [‡]	1588	1571 64b [†] 141.2 [‡]	1590	1571 64b [†] 176.5 [‡]	1600	1572 64b [†] 177.1 [‡]

^a Ref⁵⁷, [†] Irreducible representation of the involved normal mode in C_2 symmetry

These results are in concordance with the trend of the lanthanides, where the ionic radii of the trivalent lanthanide ion decrease when we move along the period, producing a bigger torsion on the macrocyclic ligand that can be seen also on the reduction of the $\angle \text{N}_{\text{imine}} - \text{C} - \text{C} - \text{N}_{\text{imine}}$ dihedral angle value. With respect to the excited state geometries, negligible changes regarding to bond lengths and angles are exhibited for all $[\text{Ln}^{\text{III}}\text{HAM}]^{3+}$ systems. From these results it can be concluded that geometrical parameters in the excited-states have non-significant conformational changes in comparison with their ground state structural data. These results allowed us to infer that due to the small structural changes between the ground and excited states we expect a small Stoke shift.

The DFT frequency calculations not only permit us to confirm a minima on the potential energy surface, also these results made us possible to validate our methodology contrasting our results with the experimental infrared spectroscopy data reported by K. Abid and D. Fenton⁵⁷; the results are summarized on Table 2, it can be seen that DFT calculations reproduce in good agreement the two infrared bands presented on all $[\text{Ln}^{\text{III}}\text{HAM}]^{3+}$ complexes, these are related with the two ($\nu_{\text{C}=\text{N}(\text{imine})}$ and $\nu_{\text{C}=\text{N}(\text{pyridine})}$) antisymmetric stretching vibrational modes of the macrocyclic ring. The difference between the experimental and calculated data for the $\nu_{\text{C}=\text{N}(\text{imine})}$ is approximately 60cm^{-1} , while for the $\nu_{\text{C}=\text{N}(\text{pyridine})}$ is 30cm^{-1} , giving an average deviation of the experimental in around 3%.

From Table 3, we can observe two distinct trends on the electronic structure; the first one related to the closed shell complexes ($[\text{LaHAM}]^{3+}$ and $[\text{LuHAM}]^{3+}$), in which is appreciated how the spherical distribution of the charge split by the crystal field. In these two systems we have the $4f^0$ and $4f^{14}$ electronic configurations on the valence region, where the symmetric distribution of the electronic charge confers a high stability to the different energy levels, having as a consequence the biggest HOMO-LUMO gap for the

studied series, 3.05 eV for $[\text{LaHAM}]^{3+}$ and 2.92 eV for $[\text{LuHAM}]^{3+}$. A simply explanation of this can be made from a MOs composition analysis of both systems, where is observed for the lanthanum complex that the latest occupied molecular orbitals are principally formed by the ligand (p_x , p_y , p_z orbitals), and the spectra of the lowest energy virtual orbitals is centered in p and f empty orbitals. The case of the Lu complex is similar to the presented before, where the frontier occupied orbitals are entirely localized on the ligand, but the virtual orbitals for this system are a mix of p , d and s orbital of the lanthanide center (Lu). The second trend involves the open shell molecules ($[\text{CeHAM}]^{3+}$ and $[\text{EuHAM}]^{3+}$), in both cases the $4f$ -shell is occupied, then the nature of the frontier orbitals have been changed with respect to the closed shell systems with the consequent reduction of the H-L gap product of the low-lying f -states. These results are schematized on the MOs energy diagram in Figure 2.

In order to understand deeply the electronic structure for the open shell molecules, we used the results obtained from the multireference calculations for the cerium complex, reported in Table 4. In this case is relatively easy to understand the effect of the electron correlation because of there is only one electron in the $4f$ -shell. The crystal-field split the f -shell in six different Kramers doublets, where the small energy difference among the states allow us to conclude that the HAM ligand produce a weak crystal field effect. On the other hand, the spin-orbit coupling introduce a strong mix between the crystal field states, giving as a consequence an increment on the energy difference (510cm^{-1}) between the ground and the first-excited state, it is almost twice of the obtained from the spin-free (SF) calculation (269cm^{-1}). The difference in energy mentioned before is slightly smaller than the energy of the spin-orbit coupling for the free ion (650cm^{-1}) indicating, firstly that the spin-orbit coupling is quenched by the bonding interaction and also the importance of the spin-orbit coupling to describe the electronic properties on this kind of complexes.

Table 3 Frontier molecular orbital (FMOs) composition based on atomic orbitals (AOs) contribution and their relative energies (eV) for all $\text{Ln}^{\text{III}}\text{HAM}^{3+}$

Closed Shell						Open Shell					
$[\text{LaHAM}]^{3+}$			$[\text{LuHAM}]^{3+}$			$[\text{CeHAM}]^{3+}$			$[\text{EuHAM}]^{3+}$		
MO	E (eV)	AOs (%)	MO	E (eV)	AOs (%)	MO	E (eV)	AOs (%)	MO	E (eV)	AOs (%)
64a	−16.012	$p_z N$ (38.4) $p_z C$ (21.9)	67a	−16.132	$p_z N$ (34.7) $p_z C$ (12.3)	62bα	−15.484	$p_z C$ (44.9) $p_z N$ (20.4) $p_x C$ (18.1)	66aα	−15.456	$f_z Eu$ (58.2) $f_z^3 Eu$ (16.6) $f_{xyz} Eu$ (15.1)
60b	−15.705	$p_y N$ (36.2) $p_x N$ (9.9)	64b	−16.119	$p_z N$ (22.7) $p_y N$ (13.9)	62bβ	−15.480	$p_z C$ (44.4) $p_z N$ (18.1)	67aα	−15.314	$p_z C$ (34.6) $p_z N$ (16.7) $f_z Eu$ (13.1)
61b	−15.651	$p_y N$ (25.9) $p_z N$ (20.2)	65b	−15.786	$p_y N$ (23.7) $p_z C$ (15.3) $p_z N$ (10.6)	65aα	−15.352	$p_z C$ (45.0) $p_z N$ (19.1) $p_x C$ (11.9)	64bα	−15.190	$f_z^2 y Eu$ (68.2) $f_z^2 x Eu$ (19.2)
62b	−15.441	$p_z C$ (47.5) $p_z N$ (19.2)	66b	−15.544	$p_z C$ (25.7) $p_z N$ (18.9) $p_y N$ (10.0)	65aβ	−15.348	$p_z C$ (45.0) $p_z N$ (19.2) $p_x C$ (12.0)	68aα	−15.171	$f_z^3 Eu$ (74.0) $f_z Eu$ (20.8)
65a HOMO	−15.311	$p_z C$ (47.3) $p_z N$ (20.6)	68a HOMO	−15.479	$p_z C$ (35.4) $p_x C$ (18.4) $p_z N$ (16.0)	66aα SOMO	−13.075	$f_z^3 Ce$ (93.2)	65bα SOMO	−15.149	$f_z^2 x Eu$ (68.6) $f_z^2 y Eu$ (16.9)
63b LUMO	−12.254	$p_z N$ (29.6) $p_z N$ (25.6) $d_{xz} La$ (15.8)	69a LUMO	−12.562	$p_z C$ (29.3) $p_z N$ (19.6) $d_{x^2-y^2} Lu$ (3.8)	63bα SUMO	−12.789	$f_y Ce$ (84.3) $f_x Ce$ (12.1)	66bα SUMO	−14.788	$f_x Eu$ (50.4)
66a	−12.224	$p_z C$ (36.5) $p_z N$ (25.9) $d_{yz} La$ (6.4)	67b	−12.361	$p_z C$ (26.7) $p_z N$ (25.0) $d_{xz} Lu$ (7.2)	67aα	−12.753	$f_z Ce$ (93.1)	66aβ	−12.237	$p_z C$ (35.3) $p_z N$ (26.3)
64b	−11.891	$p_z C$ (44.5) $p_z N$ (11.6) $f_z^3 La$ (11.2)	68b	−11.943	$p_z C$ (40.8) $p_z N$ (11.6) $d_{xz} Lu$ (2.2)	68aα	−12.744	$f_{xyz} Ce$ (94.5)	69aα	−12.216	$p_z C$ (35.1) $p_z N$ (26.1)
67a	−11.594	$p_z C$ (45.8) $p_z N$ (13.9) $f_{xyz} La$ (11.4)	70a	−11.726	$p_z C$ (40.3) $p_z N$ (13.3) $d_{xz} Lu$ (3.6)	64bα	−12.629	$f_x Ce$ (63.9)	67bα	−12.200	$p_z C$ (49.6) $p_z N$ (13.0) $d_{xz} Eu$ (10.8)
68a	−11.199	$f_z^3 La$ (47.2) $f_{xyz} La$ (18.9) $d_z^2 La$ (17.2)	71a	−11.293	$d_z^2 Lu$ (48.7) $s Lu$ (29.1)	63bβ	−12.436	$f_y Ce$ (75.5)	63bβ	−12.188	$p_z C$ (43.4) $p_z N$ (19.0)

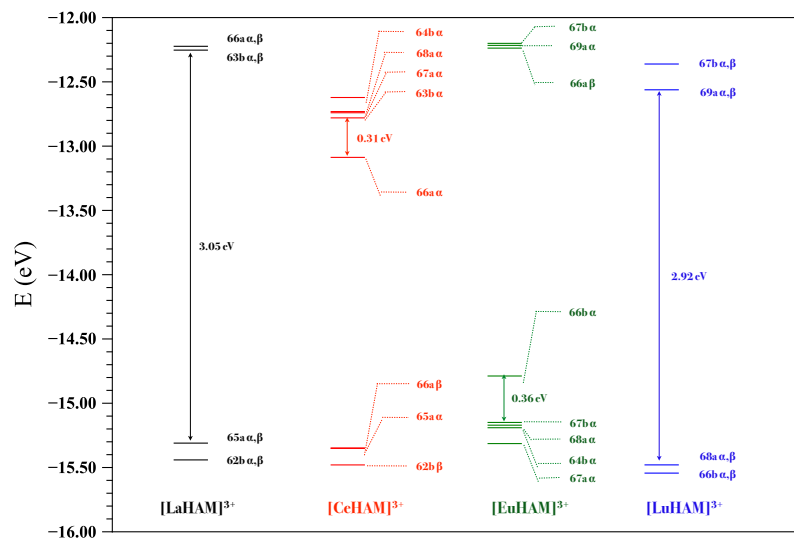


Fig. 2 Molecular orbital (MO) energy diagram for all [Ln^{III}HAM]³⁺ systems at scalar relativistic level

In the f^6 configuration for the Eu^{3+} complex, most of the SF states are highly multideterminantal, then the multi-state NEVPT2 or MRCI step mixes the SF roots and it is difficult to analyze the final states in term of orbitals. Because of that in Table S1 (see Supporting Information), we only present the energy values to show the low lying states in the different multiplicities, in this case is emphasized that the increment of the number of electrons on the $4f$ -shell introduce a large number of electronic states quite close in energy, where the first excited SF-heptuplet is only 18 cm^{-1} above the ground state, corroborating again the weak crystal field produced by the HAM ligand. A reasonable description of the electronic structure can be obtained through the net charge, spin density (on open shell molecules) and charge transfer analysis. The results pre-

sented in Table 5, show that in all cases the systems exhibit a charge transfer from the nitrogen atoms on the macrocyclic ligand toward the lanthanide center. Although the tendency for all population analysis schemes is the same, Mulliken and Hirschfeld methods underestimate the values of the charges giving only a qualitative result; Voronoi and NBO give a best description of the charge. Furthermore, spin density analysis of the open shell molecules evidence that the electronic density is centered over f orbitals on the cerium (0.97) and europium (6.03) ions, these added to the results obtained from natural electronic configuration (NEC) could confirm a 3+ oxidation state for all the lanthanide ions on the studied series and also suggest the non or negligible participation of the f orbitals on the bonding.

Table 4 Relative energies (cm^{-1}) of the electronic states for the CAS(1,7)SCF and MRCI calculations in [CeHAM]³⁺ complex

SF-State	SF-CAS(1,7)SCF	SO-CAS(1,7)SCF	Wavefunction ^b
² 0 ^a	0	0	45% ² 0 ¹ / ₂ > + 30% ² 0 ⁻¹ / ₂ > + 25% ² 2 ⁻¹ / ₂ >
² 1	269	510	18% ² 3 ⁻¹ / ₂ > + 15% ² 4 ⁻¹ / ₂ > + 13% ² 2 ⁻¹ / ₂ > + ...
² 2	452	1668	20% ² 4 ¹ / ₂ > + 20% ² 5 ¹ / ₂ > + 30% ² 4 ⁻¹ / ₂ > + ...
² 3	749	1926	25% ² 0 ¹ / ₂ > + 20% ² 1 ¹ / ₂ > + 20% ² 1 ⁻¹ / ₂ > + ...
² 4	899	2285	22% ² 2 ¹ / ₂ > + 11% ² 3 ¹ / ₂ > + 22% ² 2 ⁻¹ / ₂ > + ...
² 5	1804	2949	30% ² 5 ⁻¹ / ₂ > + 25% ² 5 ⁻¹ / ₂ > + 15% ² 4 ¹ / ₂ > + ...
² 6	3332	4644	70% ² 6 ¹ / ₂ > + 20% ² 6 ¹ / ₂ > + 10% ² 5 ¹ / ₂ >

^a The different states are represented not using any symmetry irreducible representation because of in the present case the calculations were done without symmetry. Only the number of the state is used together with the multiplicity.

^b The wavefunction represent the contribution of the different crystal field states (spin-free) to the MRCI (spin-orbit) states. The wave-function is written in terms of $\sum \Gamma_{(SF)} |m_s\rangle$ where $\Gamma_{(SF)}$ is the spin-free state and $|m_s\rangle$ is the spin projection.

Table 5 Atomic population analysis over the lanthanide center and nitrogen atoms obtained at scalar relativistic level

	Hirschfield	Mulliken	Voronoi	NBO	
				NAC ^a	NEC ^b
[LaHAM] ³⁺					
La	0.903	1.771	2.438	2.596	[Core]6s ^{0.08} 4f ^{0.11} 5d ^{0.22} 5f ^{0.01}
N _{pyr}	-0.107	-0.479	-0.451	-0.556	[Core]2s ^{1.38} 2p ^{4.17} 3p ^{0.02} 3d ^{0.01}
N _{imine}	-0.112	-0.486	-0.450	-0.593	[Core]2s ^{1.35} 2p ^{4.17} 3p ^{0.02} 3d ^{0.01}
[CeHAM] ³⁺					
Ce	0.867	1.752 (0.97) [†]	2.412	2.747	[Core]6s ^{0.09} 4f ^{0.92} 5d ^{0.25} 5f ^{0.01}
N _{pyr}	-0.105	-0.481	-0.452	-0.551	[Core]2s ^{1.38} 2p ^{4.16} 3p ^{0.02} 3d ^{0.01}
N _{imine}	-0.108	-0.486	-0.448	-0.575	[Core]2s ^{1.35} 2p ^{4.17} 3p ^{0.02} 3d ^{0.01}
[EuHAM] ³⁺					
Eu	0.891	1.769 (6.03) [†]	2.121	1.679	[Core]6s ^{0.39} 4f ^{6.09} 5d ^{0.01} 5f ^{0.02}
N _{pyr}	-0.115	-0.489	-0.419	-0.530	[Core]2s ^{1.31} 2p ^{4.18} 3p ^{0.02} 3d ^{0.01}
N _{imine}	-0.113	-0.487	-0.408	-0.473	[Core]2s ^{1.33} 2p ^{4.10} 3p ^{0.02} 3d ^{0.01}
[LuHAM] ³⁺					
Lu	0.837	1.597	2.180	2.164	[Core]4f ^{13.99} 6s ^{0.22} 5d ^{0.60} 6d ^{0.03}
N _{pyr}	-0.104	-0.483	-0.432	-0.527	[Core]2s ^{1.33} 2p ^{4.18} 3p ^{0.02} 3d ^{0.01}
N _{imine}	-0.106	-0.485	-0.466	-0.542	[Core]2s ^{1.35} 2p ^{4.16} 3p ^{0.01} 3d ^{0.01}

NAC^a : Natural Atomic Charge, NEC^b: Natural Electronic Configuration, [†] Spin density value

3.2 Bonding Nature

3.2.1 Energy Decomposition Analysis (EDA)

Related to the description of the bonding and based on the results obtained from the EDA (Table 6), we observed that in all cases the orbital interaction is greater than the Pauli's repulsion and the electrostatic interaction, that means that these systems exhibit a covalent behaviour. This covalent character is only well-defined for the [EuHAM]³⁺ complex, in which the orbital contribution is twice the electrostatic term; on the other cases the degree of covalency is less than the europium complex, since the electrostatic and the orbital terms have similar energy values as can be seen for [LaHAM]³⁺ and [LuHAM]³⁺ systems. This result put on evidence that there is no relation between the occupancy of the *f*-shell and the covalent behavior of these systems. Additionally to this, the previous results from NBO analysis (Table 5) show the non-participation of *f*-shell electrons on the bonding, since these electrons remain on the *f*-shell with an unaltered population. Nevertheless, there is a connection between the stability of the complexes, measured in terms of the bonding energy (*E*_{BE}), and the *f*-shell electrons, we observed that *E*_{BE} for the [LuHAM]³⁺ is greater than the [LaHAM]³⁺ complex, since the *f*-shell is fully occupied in the first case and empty in the second one, moreover when we move to the middle of the lanthanide series, the case of [EuHAM]³⁺, we observed that the *E*_{BE} significantly increase its value, that is due to a particular stabilization phenomena when a shell is half filled.

Table 6 Morokuma-Ziegler's energy decomposition analysis (EDA) for [Ln^{III}HAM]³⁺ complexes at scalar relativistic level in eV

	[LaHAM] ³⁺	[CeHAM] ³⁺	[EuHAM] ³⁺	[LuHAM] ³⁺
ΔE_{Pauli}	8.128	8.969	7.424	8.580
ΔV_{Estat}	-13.920	-14.258	-14.162	-15.365
ΔE_{Orb}	-18.151	-19.146	-28.610	-20.256
<i>E</i> _{BE}	-23.942	-24.435	-35.347	-27.042
%Covalency	56.6	57.3	66.9	56.9

ΔE_{Pauli} : Pauli repulsion
 ΔV_{Estat} : Electrostatic interaction
 ΔE_{Orb} : Orbital interaction
*E*_{BE} : Bonding energy.

3.2.2 Electron Localization Function (ELF) Analysis

It is a fact that the ELF is a good and useful descriptor of the chemical bonding based on the topological analysis of local quantum mechanical functions related to the Pauli's exclusion principle. We study the metal-ligand (Ln-HAM) interaction as well as a qualitative model for the interpretation of the covalent or ionic behavior on the bonding between these two fragments. In Figure 3, we show the three-dimensional representation of the ELF for all the [Ln^{III}HAM]³⁺ studied complexes, this analysis support the results of the covalent character on the Ln-HAM bond, where it can be appreciated

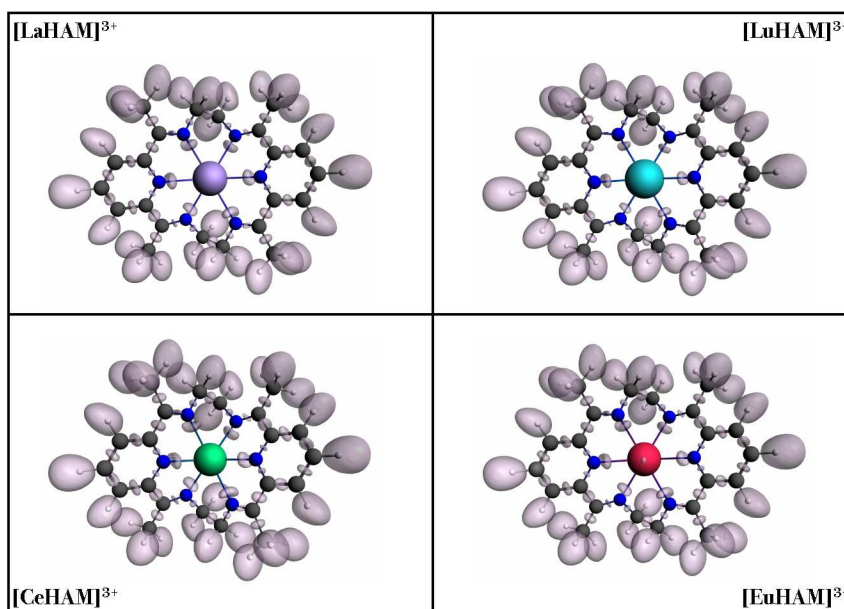


Fig. 3 3-D plot of the electron localization function (ELF) for all $[\text{Ln}^{\text{III}}\text{HAM}]^{3+}$ complexes

the presence of di-synaptic basins between the lanthanide ion and the six nitrogen atoms of the macrocycle; we defined these basins as di-synaptics due to the position between these two centers, nevertheless it looks like more as mono-synaptic basins resulting from lone-pair electrons belonging to the nitrogen atoms and is well oriented toward the lanthanide center; this allow us to suggest the existence of a dative covalent bond (coordinated bond).

3.3 Optical Properties

It is known that the luminescence from lanthanide ions is inherently weak, due to the fact that the $f-f$ electronic transitions involved are Laporte forbidden. Despite of this, the intensity of these emissions can be considerably enhanced by attaching a suitable organic ligand, which has strong light absorbance on an appropriated wavelength, specially on the ultraviolet or visible region of the spectrum making that this organic ligand works as an “antenna”, then this antenna could transfer the absorbed energy to the lanthanide centre and excite it to the emissive state increasing the luminescence. Not all lanthanide ions give rise to $f-f$ electronic transitions, that includes the obvious cases of the f^0 and f^{14} configurations that represent La^{3+} and Lu^{3+} species respectively, these can be figured out from on Table 7 and Figure 4; where we ob-

serve intense and wide absorption bands for both closed shell complexes that have been characterized in two different ways. The first type of absorption bands, and also the most intense, are found around 210-230nm for the $[\text{LaHAM}]^{3+}$ system and between 200-225nm on the case of the $[\text{LuHAM}]^{3+}$ complex. These bands arise from a π MOs strongly localized on the macrocyclic ligand with high contribution of the p_x , p_y and p_z atomic orbitals, to metal-centered MOs, with entirely character of f orbitals; in the case of $[\text{LaHAM}]^{3+}$ and d orbitals on the $[\text{LuHAM}]^{3+}$ complex; these electronic transitions are assigned as ligand to metal charge transfer (LMCT) bands. The other kind of bands are depicted as intra-ligand (IL) absorption bands, generally between p_z orbitals on the macrocycle (π MOs), these can be found in the range of 251-339nm for $[\text{LaHAM}]^{3+}$, as well as the case of $[\text{LuHAM}]^{3+}$ complex that show these IL absorption bands between 244-350 nm. These results are in good agreement with the experimental data reported by Radecka-Paryzek⁵⁸ for $\pi \rightarrow \pi^*$ high energy absorption bands on these kind of systems, obtained from diffuse reflectance spectroscopy, in the range of 243-303nm. The spin-orbit coupling (SOC) was also considered in time-dependent density functional theory (TD-DFT) calculations for closed shell systems, the results show, a slight intensity increase of the bands due to more electronic transitions (or combination of them), additionally to this a small shift no longer than ≈ 5 nm is observed for the $[\text{LuHAM}]^{3+}$ complex.

Table 7 Excitation energies (eV), oscillator strength (f) and electronic transitions calculated for closed shell [LnHAM]³⁺ (Ln=La,Lu) complexes at scalar relativistic level

[LaHAM] ³⁺						
Band	λ (nm)	E (eV)	f (x10)	Active MOs	%	Type of Transition
a	210.7	5.884	0.241	60 <i>b</i> → 69 <i>a</i>	44.2	<i>P</i> _(HAM) − <i>f</i> _(La)
				61 <i>b</i> → 69 <i>a</i>	42.6	LMCT
b	218.1	5.684	0.506	59 <i>b</i> → 68 <i>a</i>	63.2	<i>P</i> _(HAM) − <i>f</i> _(La)
				65 <i>a</i> → 66 <i>b</i>	33.3	LMCT
c	228.5	5.426	0.913	65 <i>a</i> → 65 <i>b</i>	40.1	<i>P</i> _(HAM) − <i>f</i> _(La) LMCT
d	251.8	4.924	1.116	60 <i>a</i> → 64 <i>b</i>	31.9	<i>P</i> _(HAM) − <i>P</i> _(HAM) ILCT
				58 <i>b</i> → 67 <i>a</i>	18.4	
	253.3	4.895	2.714	61 <i>a</i> → 64 <i>b</i>	18.5	
				57 <i>b</i> → 66 <i>a</i>	16.5	
254.2	4.877	1.936	62 <i>a</i> → 64 <i>b</i>	13.5		
			60 <i>a</i> → 64 <i>b</i>	41.2		
e	281.9	4.398	0.616	63 <i>a</i> → 64 <i>b</i>	17.0	<i>P</i> _(HAM) − <i>P</i> _(HAM) IL
				61 <i>a</i> → 63 <i>b</i>	16.0	
				58 <i>b</i> → 66 <i>a</i>	14.5	
	285.3	4.346	0.469	62 <i>a</i> → 63 <i>b</i>	17.0	
63 <i>a</i> → 64 <i>b</i>				14.5		
f	337.7	3.671	1.076	65 <i>a</i> → 64 <i>b</i>	40.3	<i>P</i> _(HAM) − <i>P</i> _(HAM)
	339.5	3.652	1.136	62 <i>b</i> → 66 <i>a</i>	33.5	IL
[LuHAM] ³⁺						
Band	λ (nm)	E (eV)	f (x10)	Active MOs	%	Type of Transition
a	207.9	5.963	0.103	61 <i>b</i> → 71 <i>a</i>	76.9	<i>P</i> _(HAM) − <i>d</i> _(Lu)
	213.4	5.810	0.208	65 <i>b</i> → 69 <i>b</i>	55.8	LMCT
b	221.6	5.596	0.396	64 <i>b</i> → 71 <i>a</i>	48.8	<i>P</i> _(HAM) − <i>d</i> _(Lu)
	222.0	5.584	0.430	66 <i>b</i> → 71 <i>a</i>	42.2	LMCT
c	244.6	5.069	1.089	61 <i>b</i> → 70 <i>a</i>	40.1	<i>P</i> _(HAM) − <i>P</i> _(HAM) IL
	248.1	4.997	1.157	66 <i>b</i> → 70 <i>a</i>	33.2	
				64 <i>a</i> → 68 <i>b</i>	24.5	
	252.5	4.910	1.929	63 <i>a</i> → 67 <i>b</i>	21.5	
d	268.7	4.614	0.696	62 <i>b</i> → 70 <i>a</i>	17.7	<i>P</i> _(HAM) − <i>P</i> _(HAM) IL
	269.8	4.595	0.275	64 <i>b</i> → 70 <i>a</i>	50.0	
	272.1	4.556	0.125	60 <i>b</i> → 69 <i>a</i>	70.5	
e	278.4	4.453	0.966	63 <i>a</i> → 69 <i>a</i>	55.2	<i>P</i> _(HAM) − <i>P</i> _(HAM) IL
	285.1	4.349	0.311	64 <i>a</i> → 67 <i>b</i>	37.4	
				64 <i>b</i> → 70 <i>a</i>	15.5	
	285.8	4.338	0.330	67 <i>a</i> → 68 <i>b</i>	44.6	
f	309.6	4.000	0.167	64 <i>b</i> → 70 <i>a</i>	22.5	<i>P</i> _(HAM) − <i>P</i> _(HAM) IL
				61 <i>b</i> → 69 <i>a</i>	49.1	
g	333.8	3.714	0.557	66 <i>a</i> → 67 <i>b</i>	79.8	<i>P</i> _(HAM) − <i>P</i> _(HAM) IL
				64 <i>b</i> → 69 <i>a</i>	43.2	
h	349.8	3.544	1.006	68 <i>a</i> → 68 <i>b</i>	21.5	<i>P</i> _(HAM) − <i>P</i> _(HAM) IL
				68 <i>a</i> → 67 <i>b</i>	42.2	
				66 <i>b</i> → 69 <i>a</i>	21.0	

Unfortunately, TD-DFT algorithm for open shell molecules at spin-orbit relativistic level is not yet implemented on the ADF computational code, then for open shell systems scalar relativistic TD-DFT were performed. As in the case of closed shell molecules, the Ce^{3+} and Eu^{3+} systems also present the absorption LMCT bands involving p -MOs from the ligand and purely f -MOs for cerium complexes and mixed d or f -MOs for europium systems (see Table 8), moreover these bands have a shift of around 40 nm with respect to the closed shell spectra, and also the appearance of more bands on the visible region; beside of this, the results for $[\text{EuHAM}]^{3+}$ are in agreement with the results obtained by N. Sabbatini²⁵ and J. C. Bünzli^{6,13} with respect to the characterization of these bands located around 250-330 nm. The IL absorption bands observed for close shell molecules practically disappear or get

combined with LMCT bands with low contribution in both cases. Furthermore, $f-f$ electronic transitions are found in both cases on the NIR region among 1000-1400 nm and 985-3335 nm for $[\text{CeHAM}]^{3+}$ and $[\text{EuHAM}]^{3+}$ respectively. The f^1 ion of the $[\text{CeHAM}]^{3+}$ complex exhibits two bands on the NIR, at 1002.3 and 1415 nm; unfortunately, there is not experimental and theoretical data reported of this system in reference to $f-f$ electronic transitions, but other organometallic complex like $[\text{CeCOT}_2]^{-1}$ (COT= 1,3,5,7-Cyclooctatetraene), with a Ce^{3+} ion, have been extensively studied, and calculated results showed two $f-f$ electronic transitions around 1200 and 1400nm. Even an ion like Eu^{3+} (f^6), which has several absorptions bands on the visible region, has only few weak bands on the NIR region. The absorption spectra of these complexes are presented in Figures 5 and 6.

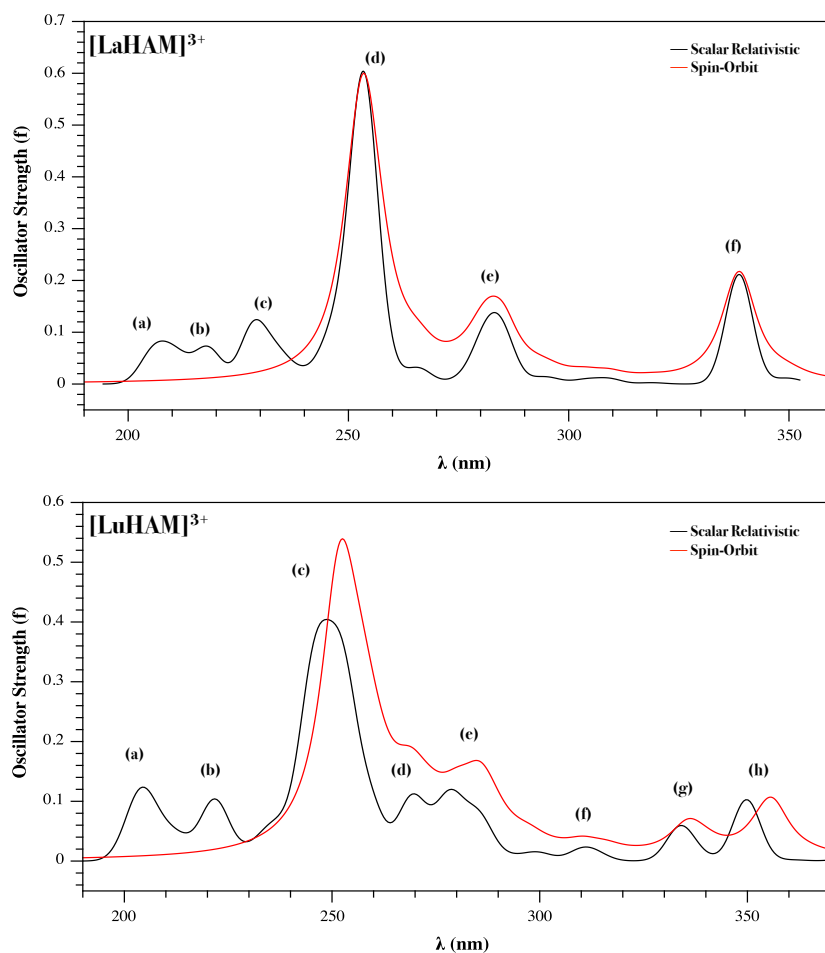


Fig. 4 Absorption Spectra for $[\text{LaHAM}]^{3+}$ and $[\text{LuHAM}]^{3+}$ complexes calculated at relativistic level with SAOP model potential

Table 8 Excitation energies (eV), oscillator strength (f) and electronic transitions calculated for open shell [LnHAM]³⁺ (Ln=Ce, Eu) complexes at scalar relativistic level

[CeHAM] ³⁺						
Band	λ (nm)	E (eV)	f (x10)	Active MOs	%	Type of Transition
a	251.8	4.923	1.962	59b α $\rightarrow$ 70a α	32.2	$P_{(HAM)} - d, f_{(Ce)}$ LMCT
				65a α $\rightarrow$ 67b α	22.5	
	253.7	4.887	1.076	58b α $\rightarrow$ 68a α	25.6	
				62a α $\rightarrow$ 64b α	25.2	
	254.3	4.876	1.172	65a α $\rightarrow$ 67b α	37.0	
b	282.4	4.390	0.439	57b β $\rightarrow$ 66a β	35.0	$P_{(HAM)} - f_{(Ce)}$ LMCT
				61a β $\rightarrow$ 63b β	24.9	
	284.5	4.358	0.216	63a α $\rightarrow$ 64b α	35.4	
				64a β $\rightarrow$ 64b β	27.3	
	287.6	4.311	0.187	62b α $\rightarrow$ 71a α	29.2	
				62a α $\rightarrow$ 63b α	19.9	
c	340.6	3.640	0.638	65a β $\rightarrow$ 64b β	60.3	$P_{(HAM)} - d, f_{(Ce)}$ LMCT
	342.2	3.623	1.019	62b α $\rightarrow$ 67a α	27.2	
				62b β $\rightarrow$ 66a β	21.1	
d	1002.3	1.237	0.055	66a α $\rightarrow$ 63b α	99.8	$f_{z^3} - f_x$
e	1415.0	0.875	0.162	66a α $\rightarrow$ 64b α	99.7	$f_{z^3} - f_y$
[EuHAM] ³⁺						
Band	λ (nm)	E (eV)	f (x10)	Active MOs	%	Type of Transition
a	247.1	5.017	1.651	63b α $\rightarrow$ 71a α	17.1	$P_{(HAM)} - d_{(Eu)}$ LMCT
	248.4	4.992	1.920	63b α $\rightarrow$ 71a α	37.7	
	250.4	4.952	2.067	63b α $\rightarrow$ 71a α	35.5	
b	335.4	3.697	1.111	62b β $\rightarrow$ 70a β	14.0	$P_{(HAM)} - d_{(Eu)}$ LMCT
				65b α $\rightarrow$ 69a α	13.5	
				65a β $\rightarrow$ 70b β	11.5	
	332.4	3.730	0.600	62b α $\rightarrow$ 69a α	23.9	
c	597.2	2.076	0.203	59a α $\rightarrow$ 66b α	95.1	$P_{(HAM)} - f_{(Eu)}$ LMCT
d	750.5	1.652	0.251	62a α $\rightarrow$ 66b α	93.1	$P_{(HAM)} - f_{(Eu)}$ LMCT
e	879.3	1.410	0.258	63a α $\rightarrow$ 66b α	83.2	$P_{(HAM)} - f_{(Eu)}$ LMCT
f	986.3	1.257	0.203	65a α $\rightarrow$ 66b α	69.9	$f_{xyz} - f_x$
g	1166.4	1.063	0.030	66a α $\rightarrow$ 66b α	92.6	$f_z - f_x$
h	1341.8	0.924	0.062	64b α $\rightarrow$ 66b α	92.8	$(f_{z^2y}, f_{z^2x}) - f_x$
i	1577.4	0.786	0.007	66a α $\rightarrow$ 66b α	96.0	$f_z - f_x$
j	3332.9	0.372	0.015	68a α $\rightarrow$ 66b α	99.8	$f_{z^3} - f_x$

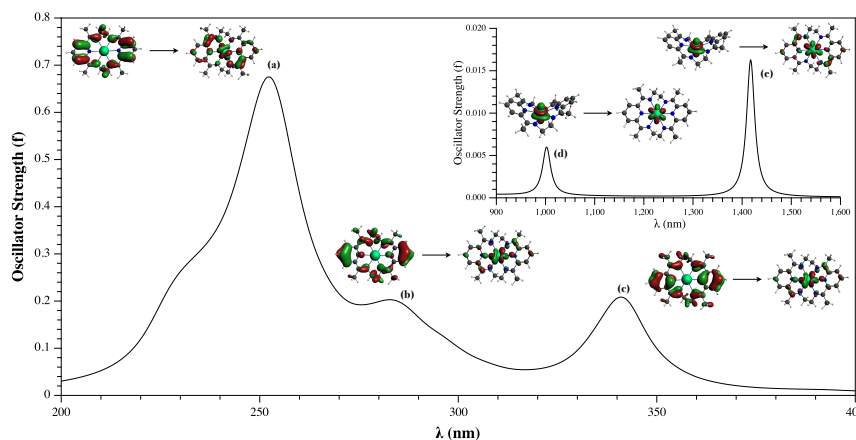


Fig. 5 Absorption Spectra for $[\text{CeHAM}]^{3+}$ complex calculated at scalar relativistic level with SAOP model potential

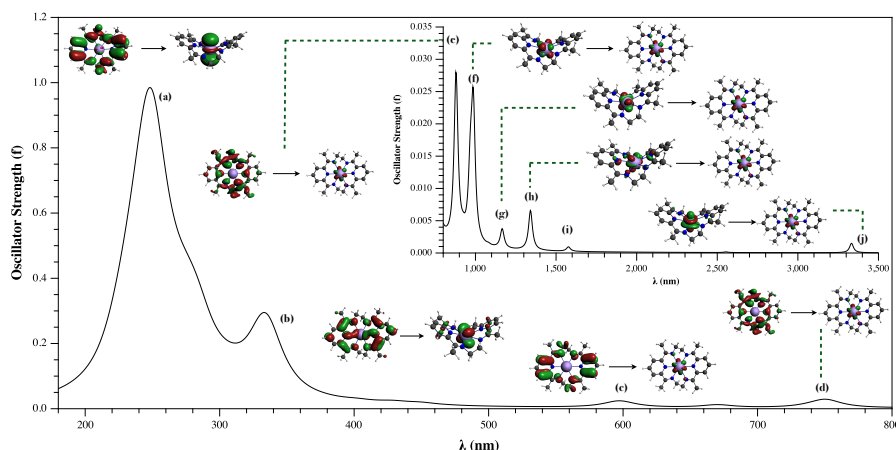


Fig. 6 Absorption Spectra for $[\text{EuHAM}]^{3+}$ complex calculated at scalar relativistic level with SAOP model potential

4 Conclusions

The results obtained in this work reproduce with high accuracy the experimental data reported for these complexes (crystallographic, infrared spectra and UV-Vis spectra) and from the point of view of the electronic structure describe properly the trend of the f -shell on the lanthanide series. Furthermore the results show that the interaction between the macrocyclic ligand and the trivalent lanthanide ion is mainly covalent in all cases, giving the following tendency of covalence increase as follows: $[\text{LaHAM}]^{3+} < [\text{LuHAM}]^{3+} < [\text{CeHAM}]^{3+} < [\text{EuHAM}]^{3+}$; this fact is supported by the Morokuma-Ziegler's EDA and the ELF analysis, which allowed us to suggest a kind of dative covalent interaction between these two fragments. The TDDFT study shows that the absorption spectra on the

ultraviolet and visible region are in good agreement with the experimental data previously reported and are characterized in the same way as the experiment assigned these bands for both closed and open shell systems. Additionally, these complexes exhibit three fundamental characteristics that could let possible the energy transfer phenomena required in a molecular antenna, these are: the existence of ligand to metal charge transfer (LMCT) electronic transitions on the ultraviolet and visible region, the electronic charge transfer (from nitrogen atoms on the macrocyclic ring to the trivalent lanthanide center) and also the orbital overlap from the covalent interaction. Also, these lanthanide hexa-aza macrocyclic complexes exhibit the expected NIR $f-f$ electronic transitions for the open shell complexes, which can allow us to suggest these lanthanide macrocyclic systems as a promising optical sensitizer molecular antenna.

5 Acknowledgments

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