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

Walter A. Rabanal-León<sup>‡</sup>, Dayán Páez-Hernández and Ramiro Arratia-Pérez<sup>†</sup>

Universidad Andrés Bello, Ph.D Program in Molecular Physical Chemistry, Relativistic Molecular Physics (ReMoPh) Group, Av. República 275 2do Piso, Santiago, CHILE.

## Supporting Information

### Overview

- 1. Wavefunction calculations: Computational details
- 2. Wavefunction calculations: CASSCF results for  $[{\rm EuHAM}]^{3+}$  system

 $^{\dagger} {\bf Corresponding}$  Author:

Ramiro Arratia-Pérez Fax: +562 2770 3352

Email:

<sup>†</sup>rarratia@unab.cl (R.A.P.)

 $<sup>^{\</sup>ddagger}$ w.rabanalleon@uandresbello.edu (W.A.R.L)

#### **1** Wavefunction calculations: Computational Details

For the open-shell molecules ( $Ce^{3+}$  and  $Eu^{3+}$  cases), another kind of theoretical methods were also employed. Particularly, for a good description of the electronic states in the lanthanide series is necessary take into account not only the relativistic effect (scalar and SOC) but also the electronic correlation. In the present work, the multi-reference approach via the Complete Active Space Self Consistent Field (CASSCF) approximation was used. All these calculations were done with the ORCA 3.0 suite of programs, 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.

For the correlated calculations, a def2-TZVP quality basis set was used for all atoms with the corresponding auxiliary basis sets. For the  $[EuHAM]^{3+}$  system, four different multiplicities have been taken into account, the heptuplet (ground-state), and also quintuplet, triplet and singlet states higher in energy. Here is interesting to evaluate the effect of the different multiplicities on the properties of the ground-state and is crucial for a correct assignment of the electronic transitions in these molecules. The assignation is in general a problematic situation because of the numerous absorption lines and bands typical of the elements studied here. The scalar relativistic effects are taken into account by means of the Douglas-Kroll-Hess transformation. The spin-orbit coupling (SOC) and spin-spin coupling (SSC) were calculated very accurately using a wave function obtained from a multiconfigurational calculation of a multireference type such as MRCI.

### 2 Wavefunction calculations: CASSCF results for $[EuHAM]^{3+}$

Mult.	SF-CAS(6,7)SCF	SO-CAS(6,7)SCF
7	0.	0.
7	18.	40.
7	494.	520.
7	566.	590.
7	734.	860.
5	2029.	2000.
5	2043.	2300.
5	2130.	2450.
3	3176.	3200.
1	3354.	3679.
3	3985.	4560.
3	5090.	6079.
3	5167.	6905.
5	5703.	7380.
5	5907.	7678.
5	6118.	8950.

Table 1: Relative energies in  $\text{cm}^{-1}$  of the CAS(6,7)SCF calculations for [EuHAM]<sup>3+</sup> complex.