Synthesis, structure, theoretical studies and luminescent properties of a ternary erbium(III) complex with acetylacetone and bathophenanthroline ligands

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Abstract

A novel erbium(III) complex with acetylacetone (Hacac) and bathophenanthroline (4,7-diphenyl-1,10-phenanthroline, bath) ligands, formulated as $[\text{Er}(\text{acac})_3(\text{bath})]$, has been characterized by elemental analysis, X-ray diffraction, thermogravimetric analysis, Fourier transform infrared spectroscopy, Raman spectroscopy, absorption and emission spectroscopies. In the theoretical part of this study, semi-empirical quantum chemistry methods using AM1, PM3, PM6 and PM7 models have been employed to predict the structure of the complex, calculate the geometric and crystallographic parameters, and make comparisons with spectroscopic data using INDO/S-CI calculations. Real-time time-dependent density-functional theory (TDDFT) has also been used to calculate the optical absorption spectrum of the complex in the gas phase.

Keywords: β -diketonate; erbium(III); MOPAC; Sparkle; TDDFT.

1. INTRODUCTION

Different approaches for the design of lanthanide coordination compounds as potential precursors for electroluminescent device thin films have been proposed [1]. In fact, formation of mixed ligand complexes is a well-known methodology so as to modify the different properties of lanthanide compounds. The composition and the structure of such compounds strongly depend on the electronic features of the ligands. In this respect, it is very important to analyse the changes in structural parameters, bond energies and other properties of lanthanide complexes as a function of ligand types. A solution to these tasks lies in combining experimental and theoretical characterization resources. In theoretical chemistry, the ability to predict geometries of lanthanide complexes is fundamental in the design of luminescent complexes, for which theoretical models such as Sparkle [2], the combined quantum mechanical/molecular mechanical (QM/MM) technique [1,3] and the universal force field for the MM part have been successfully used so as to model the structures and properties of β -diketonate-based lanthanide complexes. As a counterpart to this

theoretical approach, our research team has set the goal of conducting an experimental study on the structure and properties of erbium β -diketonate-based mixed ligand complexes with N,N-donor molecules [4-11].

The choice of β -diketonates amongst the various strategies aimed at improving lanthanide luminescent quantum efficiencies discussed in the literature [12] is supported by their wide commercial availability and by their remarkable synthetic versatility. In this study the simplest β -diketonate (acetylacetonate, acac), where the substituents on both carbonyl groups are methyl groups, has been chosen to exemplify the numerical techniques. Nevertheless, the substitution of these CH_3 groups by other groups would allow to control and enhance the properties of the corresponding rare-earth complexes (for instance, branched alkyl chains are known to increase the solubility in organic solvents and the volatility, perfluorinated alkyl groups increase the Lewis acidity, aromatic substituents increase the light absorption in comparison to aliphatic substituents, etc.). Such flexibility has allowed the successful application of analogous erbium(III) complexes as, for example, active layers in organic light-emitting diodes [13], as dopants in liquid-crystals aimed at LCDs [14] or in other matrices with a view to optical amplification [15-20].

With regard to the role of the N,N-donor ligands, they act as Lewis bases and complete the rare-earth ion's first coordination sphere. Two very popular diimides are 1,10-phenanthroline (phen) and 2,2'-bipyridine (bipy). In the novel complex reported herein, bathophenanthroline (bath) has been chosen instead. Being more basic than phen ($\text{pK}_a=4.27$) or bipy ($\text{pK}_a=4.38$), bath ($\text{pK}_a=4.67$) would be expected to contribute more electron density through Er-N bond making the Er^{3+} ion more electron rich. As a result, the Er^{3+} will show less attraction for electron donor solvents. The rigidly planar structure of bath would also be helpful in obstructing the coordination of solvent molecules to inner coordination sphere of Er^{3+} and restricting the complex-solvent interaction [21]. This should help to decrease non-radiative losses. Secondly, the bulkier and more rigid planar structure of bathophenanthroline should cause a higher intensity of the sensitized luminescence, because such structure allows a better energy transfer [21-24].

In this paper, the erbium(III) complex formulated as $[\text{Er}(\text{acac})_3(\text{bath})]$, has been thoroughly characterized by elemental analysis, X-ray diffraction, thermogravimetric analysis, Fourier transform infrared spectroscopy, Raman spectroscopy, absorption spectroscopy and luminescence in solid state. Part of this data has then been used as a reference in order to evaluate the suitability of several semi-empirical calculation methods for predicting the equilibrium energy configuration and –in combination with INDO/S method and CIS- the electronic properties of the complex. Finally, a comparison with more computationally-intensive TDDFT calculations for the optical absorption spectrum has been conducted.

2. EXPERIMENTAL AND COMPUTATIONAL METHODS

2.1. Materials, synthesis and analytical data

All reagents and solvents employed were commercially available and used as supplied without further purification. All the procedures for complex preparation were carried out under nitrogen environment and using dry reagents to avoid the presence of water and oxygen, which can quench metal photoluminescence (PL).

Tris(acetylacetonate)mono(bathophenanthroline)erbium(III), $[\text{Er}(\text{acac})_3(\text{bath})]$, was obtained by mixing of equimolar quantities of methanol solutions of erbium(III) 2,4-pentanedionate [erbium(III) acetylacetonate hydrate 97%, CAS No. 70949-24-5, Sigma Aldrich] (0.464 g, 1 mmol) and bathophenanthroline [4,7-diphenyl-1,10-phenanthroline 97%, CAS No. 1662-01-7, Sigma Aldrich] (0.332 g, 1 mmol). The mixture was heated to 75 °C and stirred overnight, then washed with dioxane, and finally dried in vacuum to give the product in 86.2% yield (based in Er). Crystals

suitable for X-ray analysis were obtained by slow evaporation of a methanol-dioxane solution at room temperature (RT).

Chemical formula: $C_{39}H_{37}ErN_2O_6$. M_w : 796.98. Anal. Calcd. For $C_{39}H_{37}ErN_2O_6$: C, 58.77; H, 4.68; Er, 20.99; N, 3.51; O, 12.05. Found: C, 58.81; H, 4.66; N, 3.45%.

2.2. Physical and spectroscopic measurements

C, H, N elemental analyses were conducted using a Perkin Elmer CHN 2400 apparatus.

Differential scanning calorimetry (DSC) data were obtained on a DSC TA instrument mod Q100 v.9.0 with a heating rate of $10^\circ\text{C}/\text{min}$ under a N_2 atmosphere. Thermogravimetric and differential thermal analyses were carried out in an inert atmosphere with a Perkin Elmer STA 6000 Simultaneous Thermal Analyzer, by heating 7 mg of sample in a slow stream of N_2 (20 mL/min) from room temperature up to 800°C , with a heating rate of $20^\circ\text{C}/\text{min}$.

Infrared spectrum was recorded with a Thermo Nicolet 380 FT-IR spectrometer in KBr pellets.

Raman spectrum was recorded with a FT-Raman Bruker FRA106 by using a near-IR (Nd:YAG, 1064.1 nm) laser to excite the sample.

The crystal structure was elucidated by X-ray diffraction analysis. Prior to structural characterisation, the powder diffractogram of the erbium complex was obtained using an ENRAF-NONIUS powder diffractometer (Deby-Scherrer geometry) equipped with an INEL CPS120 detector and a quartz monochromator selecting the Cu $K\alpha_1$ wavelength (transmission geometry, capillary of 0.3 mm diameter).

For the determination of crystal structure by X-ray diffraction, a crystal of $[Er(acac)_3(bath)]$ was glued to a glass fibre and mounted on a Bruker APEX II diffractometer. Diffraction data was collected at room temperature 293(2) K using graphite monochromated $MoK\alpha$ ($\lambda=0.71073 \text{ \AA}$). Absorption corrections were made using SADABS [25]. The structure was solved by direct methods using SHELXS-97 [26] and refined anisotropically (non-H atoms) by full-matrix least-squares on F^2 using the SHELXL-97 program [26]. PLATON [27] was used to analyse the structure. Mercury version 3.1 [28] was used for figure plotting. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for this material should quote the full literature citation and the reference number CCDC 966774.

The optical absorption spectrum of the product in the UV-Vis region was recorded with a Hitachi U-2010 spectrophotometer in methanol diluted solutions (10^{-5} and 10^{-3} M). The absorbance in the NIR range was recorded using a Varian 660-IR FT-IR spectrometer in 10 wt% KBr pellet.

Steady state luminescence and excitation spectra for the samples in powder form were collected with a Jobin Yvon Fluorolog 3 spectrofluorometer equipped with a liquid nitrogen cooled InGaAs detector. The PL spectrum was recorded upon excitation at 350 nm and at $^2H_{11/2}$ ($\lambda_{exc}=532 \text{ nm}$) Er^{3+} absorption with a 450W Xenon lamp and a 500 mW continuous laser, respectively. The spectrum was acquired in the 850–1600 nm range with 1 s integration time at 1 nm steps. The NIR luminescence decay curve was measured upon excitation of the Er^{3+} ions at 980 nm with a Spectra Physics Quanta-Ray MOPO-730 laser system. The emitted light was dispersed using a single-grating 0.34 m focal length spectrometer (Spex 340E) and detected with a Peltier-cooled, NIR-extended photomultiplier (Hamamatsu H9170-75) and a lock-in amplifier. The lifetime was measured by using a digital oscilloscope (Tektronix TDS520). The optical absorption and photoluminescence spectra have been measured at room temperature and have been corrected by the spectral response of the experimental setups.

2.3. Computational methods

2.3.1. Semi-empirical calculations

Using the experimental crystallographic data as an initial guess, the ground state geometries and the corresponding vibrational frequencies were obtained using the Sparkle/AM1 [29,30], Sparkle/PM3 [31], Sparkle/PM6 [32,33] and Sparkle/PM7 [34,35] models implemented in the MOPAC2012 software [36]. The computations were performed on a server with four AMD Opteron 16 Core processors and 128 GB of memory and a Linux operating system. No imaginary vibrational frequencies were found for any of the optimized geometries.

The electronic spectra for each of the optimized structures were calculated using the ORCA electronic structure package version 2.9.1 [37,38] via the intermediate neglect of differential overlap/spectroscopic (INDO/S) method and configuration interaction with singles (CIS) [39,40] replacing the Er^{3+} ion with a point charge as described by Andrade *et al.* [41]. Triplet excited states have also been calculated for the PM7 optimized geometry using the CIS module in ORCA software package.

Semi-empirical calculations were also performed in order to optimize the solid crystalline structures using a treatment of periodic boundary conditions [39] in the MOPAC2012 software [36]. In all the calculations, we used the keywords SPARKLE XYZ and GNORM=1: the Sparkle model to treat the Er^{3+} ions, Cartesian coordinates, and the same exit criteria (when the gradient norm drops below 1.0) reported by Oliveira *et al.* [42]. We replicated the crystallographic unit cell l , m and n times along the Cartesian axis x , y and z , respectively. In each case, the keyword MERS=(l,m,n) was used, where l , m and n could be either 1 or 2 in each calculation.

2.3.2. TDDFT calculations

We employed real-time time-dependent density-functional theory [43] (TDDFT) as implemented in the OCTOPUS code [44,45] to calculate the optical absorption spectrum of $[\text{Er}(\text{acac})_3(\text{bath})]$ in the gas phase. In real-time TDDFT, the time-dependent Kohn-Sham equations are used to propagate the ground-state wavefunctions up to some finite time, thus allowing the determination of any observable of the system as a function of time. The optical absorption cross-section $\sigma(\omega)$ is related to the imaginary part of the dynamical polarizability $\alpha(\omega)$:

$$\sigma(\omega) = \frac{4\pi\omega}{c} \Im\{\langle\alpha(\omega)\rangle\} \quad (1)$$

where the brackets denote orientational averaging. In order to obtain the optical absorption spectra, a dipolar perturbation:

$$\delta v(\mathbf{r}, t) = -E_j x_j \delta(t) \quad (2)$$

that acts at $t = 0$ and equally excites all the frequencies of the system was applied, and we kept track of the dipole moment of the system as a function of time:

$$\mathbf{p}(t) = \int d\mathbf{r} \mathbf{r} n(\mathbf{r}, t) \quad (3)$$

where $n(\mathbf{r}, t)$ is the time-dependent electronic density. The components of the polarizability tensor are then simply obtained by Fourier transforming the induced dipole:

$$\alpha_{ij}(\omega) = \frac{\delta p_i(\omega)}{E_j}$$

The ground state of $[\text{Er}(\text{acac})_3(\text{bath})]$ was obtained using standard density-functional theory, also as implemented in the code OCTOPUS. This code solves the (time-independent) Kohn-Sham equations on a real space grid, using pseudopotentials to get rid of the core electrons of the atoms.

The Atomic Pseudopotentials Engine (APE) code [46] was used in order to obtain norm-conserving pseudopotentials of the Troullier-Martins type [47] for all the elements in the calculation.

In OCTOPUS, all the relevant functions are discretized in a real-space regular rectangular grid, and we chose the simulation box to be composed of spheres around each atom. Therefore, there are essentially two parameters that control the convergence of the spectra: the grid spacing and the radius of the spheres.

A uniform spacing of 0.20 atomic units and a sphere radius of 20 atomic units for Er^{3+} were used (the other elements' sphere radii were set at the default values of OCTOPUS for each element). The self-consistent electronic cycle was considered to have reached convergence when all the eigenvalues of the occupied states calculated in two consecutive iterations differed by less than 5.10^{-7} atomic units. These parameters also meant that the absorption spectra were converged to better than 0.1 eV. As for the choice of exchange and correlation functional we opted for the Perdew-Zunger [48] parameterization of the Local Spin Density approximation for both the ground state calculation and the time propagation. LSD is not the best choice for the optimization of the ground state geometry, but the structure was not re-optimized: all the calculations were done using the XRD unrelaxed geometry. For the calculation of the linear response, TDDFT requires only the exchange and correlation potential and not the energy, and this quantity is practically the same along the most popular approximations for exchange and correlation. This justifies the use of LSD also for the time propagation.

The spectra were obtained propagating the time-dependent Kohn-Sham equations for 180 atomic units of time, in time steps of 0.01 atomic units. As this propagation was not long enough to get sharp peaks from the Fourier transform of the dipole moment, we also used compressed sensing [49] in the analysis of the propagation.

3. RESULTS AND DISCUSSION

3.1. Structural description

$[\text{Er}(\text{acac})_3(\text{bath})]$ crystallizes in the triclinic space group $P-1$, with cell parameters $a=11.8685(2)$ Å, $b=12.1053(3)$ Å, $c=14.2355(3)$ Å, $\alpha=96.6630(10)^\circ$, $\beta=105.0080(10)^\circ$, $\gamma=110.1770(10)^\circ$, $V=1806.05(7)$ Å³ (Figure 1, Table 1). The lanthanide ion is eight-coordinated by six O atoms from the acetylacetonate anions and two N atoms from the bathophenanthroline molecule, forming a distorted square-antiprismatic structure in which the set N1, N2, O3, O4 and the set O1, O2, O5, O6 form two approximate squares, respectively (Figure 1). The trivalent erbium ion lies approximately in the middle of the antiprism with a distance of 1.39 Å to the face containing the N atoms and 1.19 Å to the opposite face containing exclusively oxygens. The angle between the least-squares planes of the square faces is just 2°. The Er–N distances are 2.545(2) and 2.550(2) Å and the Er–O distances are in the range 2.289(2)-2.313(2) Å. The N–Er–N bite angle is 63.6°. Selected geometric parameters are given in Table 2.

Figure 1. A perspective view of the eightfold coordination polyhedron of $[\text{Er}(\text{acac})_3(\text{bath})]$, possessing a distorted square-antiprismatic geometry. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

The six-membered chelate rings formed by Er^{3+} and the acetylacetonate ligands possess nearly planar geometries. The chelating ring associated with bathophenanthroline also possesses nearly planar geometry. The slight distortion of the β -diketonate rings occurs along the axis connecting the two oxygen atoms of the ligand. The bathophenanthroline molecules are not planar, as the terminal phenyl rings are rotated $61.36(15)$ and $70.29(17)^\circ$ with respect to the central phenanthroline unit.

The comparison of Er-O bond lengths in $[\text{Er}(\text{acac})_3(\text{bath})]$ with the corresponding bonds lengths in $[\text{Er}(\text{acac})_3]$ is directly related to the interactions of this mono ligand complex with the additional ligand, bathophenanthroline, whose introduction in the coordination sphere of erbium stimulates redistribution of electronic density in the ternary complex. The Er-bath bonding is not purely electrostatic and its formation is accompanied by a decrease in the Er-acac bond energy. Consequently, the Er-O bond lengths in $[\text{Er}(\text{acac})_3(\text{bath})]$ are larger than that in $[\text{Er}(\text{acac})_3(\text{H}_2\text{O})_2]$ [50,51]. The coordination geometry of $[\text{Er}(\text{acac})_3(\text{bath})]$ is very similar to that found in the related complex $[\text{Er}(\text{acac})_3(\text{phen})]$ [52]. In $[\text{Er}(\text{acac})_3(\text{phen})]$ the Er-N distances are $2.523(5)$ and $2.568(5)$ Å, with a N-Er-N bite angle of 64.3° and the Er-O distances range from $2.287(4)$ to $2.324(4)$ Å.

Figure 2. Packing diagram of [Er(acac)₃(bath)]

Table 1. Crystal data and structure refinement

Complex	[Er(acac) ₃ (bath)]
Empirical formula	C ₃₉ H ₃₇ ErN ₂ O ₆
Formula weight	796.97
Temperature	293(3) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i>	11.8685(2) Å
<i>b</i>	12.1053(3) Å
<i>c</i>	14.2355(3) Å
α	96.6630(10) °
β	105.0080(10) °
γ	110.1770(10) °
Volume	1806.05(7) Å ³
<i>Z</i>	2
Density (calculated)	1.466 g cm ⁻³
Absorption coefficient	2.370 mm ⁻¹
<i>F</i> (000)	802
Crystal size	0.26×0.18×0.10 mm ³
θ range for data collection	1.93–30.64°
Index ranges	−17< <i>h</i> <17; −17< <i>k</i> <17; −20< <i>l</i> <20
Reflections collected	46456
Independent reflections	11070
Completeness to 2 θ =55°	99.9%
Refinement method	Full matrix LS on <i>F</i> ²
Data/restraints/parameters	9229/0/439
Goodness-of-fit on <i>F</i> ²	1.047
Final <i>R</i> indices [<i>I</i> >2 σ (<i>I</i>)]	<i>R</i> =0.0276; <i>wR</i> =0.0651
<i>R</i> indices (all data)	<i>R</i> =0.0401; <i>wR</i> =0.0724
Largest diff. peak and hole	−0.549/1.132

Table 2. Selected distances and angles (Å,°)

Bond	Distance	Bonds	Angle
Er1–N1	2.550(2)	O1–Er1–O5	78.27(7)
Er1–N2	2.5454(19)	O1–Er1–O4	82.78(8)
Er1–O1	2.3038(18)	O5–Er1–O3	81.08(7)
Er1–O2	2.2897(19)	O4–Er1–O2	80.29(8)
Er1–O3	2.3114(18)	O3–Er1–O2	141.78(7)
Er1–O4	2.306(2)	O1–Er1–N1	146.72(6)
Er1–O5	2.2890(19)	O6–Er1–N1	77.17(8)
Er1–O6	2.313(2)	O6–Er1–N2	68.90(7)
Er1–N avg.	2.548	O5–Er1–N2	134.02(7)
Er1–O avg.	2.302		

3.2. Assessment of the accuracy of semi-empirical quantum chemistry methods

The comparison between the results obtained with the four models studied reveal that a substantial improvement in accuracy is obtained with the most recent Sparkle/PM7 model [34,35]. With this model, the unsigned mean error (UME) in the calculations for a single unit cell is $UME_{a,b,c}=0.89\%$ for the a , b and c parameters and $UME_{\alpha,\beta,\gamma}=0.39\%$ for the α , β and γ parameters. For Sparkle/AM1, $UME_{a,b,c}=7.61\%$ and $UME_{\alpha,\beta,\gamma}=3.12\%$; for Sparkle/PM3 $UME_{a,b,c}=0.97\%$ and $UME_{\alpha,\beta,\gamma}=3.32\%$; and for Sparkle/PM6 $UME_{a,b,c}=2.82\%$ and $UME_{\alpha,\beta,\gamma}=1.39\%$ were obtained. Regarding the percent error for the volume, it was 25.5% for Sparkle/AM1, 3.60% for Sparkle/PM3, 6.82% for Sparkle/PM6 and 2.01% for Sparkle/PM7.

The size of the unit cell, having a minimum dimension larger than 8 Å, guarantees enough accuracy of the calculations according to the criteria given by Stewart [53]. Nevertheless, we repeated the calculations with $2\times1\times1$, $1\times2\times1$, $1\times1\times2$, $2\times2\times1$ and $2\times2\times2$ unit cells. In all cases, the results were consistent with those for the $1\times1\times1$ case (see supplementary information, Tables S1 to S6) with very similar values of $UME_{a,b,c}$ and $UME_{\alpha,\beta,\gamma}$ for each model at all computation sizes. For the two largest computations with $2\times2\times1$ and $2\times2\times2$ unit cells, the results from the $1\times1\times1$ computations for each model were used as pre-optimized initial conditions, which permitted a significant speedup of the calculations. In these two largest cases, either with or without pre-optimization, the PM7 calculations showed worse behavior and failed to converge within the allowed time.

Apart from these accuracy considerations, it should also be noted that there are significant differences in the single-processor computation times, which range from 2 hours 11 minutes for Sparkle/AM1 to only 16 minutes for Sparkle/PM7 (for a single unit cell). These differences in the running times increase with the number of unit cells (e.g. for $2\times1\times1$, Sparkle/AM1 requires 8 hours 33 minutes, Sparkle/PM3 needs 12 hours 14 minutes and Sparkle/PM6 takes 6 hours 14 minutes, while Sparkle/PM7 requires only 1 hour 38 minutes). Consequently, Sparkle/PM7 not only provides higher accuracy than the other semi-empirical methods, but proves to be much faster.

We present now a more detailed comparison between the Sparkle/PM7 and crystallographic structures (see Figure 3) because the Sparkle/PM7 structure has the smallest difference from the experimental one.

Figure 3. Comparison of the Sparkle/PM7 optimized geometry (*green*) with the X-ray geometry (*blue*) of the complex $[\text{Er}(\text{acac})_3(\text{bath})]$ (software used for visualization: VMD version 1.9.1) [54].

The calculated Er–N distances, 2.471 and 2.473 Å, are slightly shorter than the experimental [2.545(2) and 2.550(2) Å]. The same trend is observed in the calculated Er–O distances that lie in the 2.286–2.302 Å range. The N–Er–N bite angle is 66.0°, differing only 4% from the experimental value [63.6°]. In the Sparkle/PM7 optimized geometry the terminal phenyl rings are rotated 73.68 and 74.20° from the least squares plane of the phenanthroline unit. Overall, there is a good agreement between the experimental and the Sparkle/PM7 optimized geometry.

3.3. X-ray powder diffraction

A Rietveld refinement [55] was performed with Fullprof software [56] using the powder-diffraction data measured at room temperature. The overall parameters such as cell parameters, 2θ zero, scale factor, full-width at half-maximum and asymmetry parameter were allowed to refine in the range of 5 to 50°, with a final Bragg reliability factor of 14.4%. The good agreement between experimental and calculated patterns (see Figure 4) confirms the high purity of the sample.

Figure 4. Results from a least-squares fit using the Rietveld method: experimental powder diffraction pattern (*green*); simulated diffraction pattern using the Rietveld method (*dark-blue*); difference between the observed and calculated intensities (*red*), and corresponding Bragg positions (*blue*).

3.4. Thermal analysis

The TG, DTG and DSC curves for the studied complex, [Er(acac)₃(bath)], are depicted in Figure 5. The DSC shows an endothermic effect at 248 °C, in agreement with the melting points reported for the analogous [Tb(acac)₃(phen)] and [Eu(acac)₃(phen)] by Melby *et al.* [57]. As the temperature is further increased, partial decomposition (loss of bathophenanthroline ancillary ligand) takes place in two steps (evinced by two sharp DTG peaks at 283 and 369.6 °C), with a weight loss of ca. 40% (calcd. weight loss for bath is 41%). Above this temperature, gradual removal of acetylacetonate units takes place. At 800 °C, the decomposition of the complex reaches ca. 50% weight loss, while that required for conversion into Er₂O₃ would be 78%.

For comparison purposes, it is worth noting that aforementioned loss of the N,N-donor takes place at higher temperatures than those reported for analogous [Pr(acac)₃(phen)] and [Nd(acac)₃(phen)], in which the partial decomposition ends at 315-320°C [58,59]. Thus, the bath complex is thermally more stable over its phen analogues, which in turn are more stable than their bpy ones [58,59]. The reason for this could be related to the rigidly planar nature of bath.

Figure 5. TG/DTG and DSC data for [Er(acac)₃(bath)] complex.

3.5. Vibrational characterization

3.5.1. Infrared spectroscopy

The FTIR spectrum (Figure 6) shows absorption bands with diverse intensities in the fingerprint region which correspond to main vibrations of bathophenanthroline and the acetylacetonate anions [60]. The carbonyl stretching frequency of the keto form of the ligand acac should appear at 1728 cm⁻¹, while that of the enol form should appear at 1625 cm⁻¹. These bands have been shifted to lower wavenumbers in the complex (1620 and 1599 cm⁻¹) indicating the involvement of carbonyl oxygen in the complex formation with the Er³⁺ ion. Furthermore, the red shift observed in the C=N stretching frequencies of nitrogen donors (at 1519 cm⁻¹ in the complex) shows the involvement of heteroaromatic nitrogen in the complex formation with the Er³⁺ ion [61].

Of particular interest is the series of absorption bands that are characteristic of the coordinated bathophenanthroline ancillary ligand and which appear at 764, 743, 703, 629 and 575 cm⁻¹. It is also noteworthy that the band shown at 834 cm⁻¹ (an aromatic CH out-of-plane bending vibration) is appreciably red shifted (*vs.* that of free ligand) due to the perturbation induced by the coordination of this ligand to the Er³⁺ ion [62]. The band that appears at around 575 cm⁻¹, which should be assigned to a ν(Er-N) vibration, also offers evidence of the fact that the coordination bonds have been formed between erbium and bathophenanthroline [63].

Finally, the low and broad absorption in the region 3500-2900 cm^{-1} corresponds to O-H vibrations (due to atmospheric water absorption by KBr) and C-H vibrations.

Figure 6. FTIR spectrum of $[\text{Er}(\text{acac})_3(\text{bath})]$

3.5.2. Raman spectroscopy

The Raman spectrum of the complex (Figure 7) shows a strong multiple peak at 1600 cm^{-1} , attributed to the C=N and C=O bonds from coordinated bathophenanthroline and the acetylacetonate anion. Peaks at 1446 cm^{-1} [$\nu(\text{C}=\text{C}, \text{C}=\text{N})$], at 1396 cm^{-1} [$\nu(\text{C}=\text{C}) + \delta(\text{CH})$] and near 700 cm^{-1} [$\delta(\text{CH})$] are also characteristic of coordinated bathophenanthroline. Unassigned characteristic peaks of coordinated bathophenanthroline appear at 1290 and at 1000 cm^{-1} .

The Raman-active peaks at approximately 408 cm^{-1} and that at 258 cm^{-1} can be tentatively assigned to $\nu(\text{Er-N})$ modes.

Figure 7. Raman spectrum of $[\text{Er}(\text{acac})_3(\text{bath})]$

3.6. Absorption spectra

3.6.1. Experimental absorption spectra

Figure 8 (left) shows the absorption spectrum in a 10^{-5} M methanol diluted solution. The absorption spectrum is dominated by spin allowed $\pi-\pi^*$ transitions of the β -diketone and bathophenanthroline in the ultraviolet-visible region, with a maximum at $\lambda=280$ nm [61,64].

Absorption bands of Hacac and bath are red shifted in the complex and show stabilization of the ligand orbitals after complex formation [65]. Nonetheless, the spectral shapes of the complex and free ligands in solution are pretty similar, suggesting that the coordination of the Er^{3+} ion does not have a significant influence on the $\pi-\pi^*$ state energy [65].

Increasing the solution concentration up to 10^{-3} M allows us to observe that the complex also exhibits the typical parity-forbidden narrow absorption bands, which originate from ground state $^4\text{I}_{15/2}$ to the various excited states of Er^{3+} ion, overlapped with the organic ligands absorption (Figure 8, *inset*). The transitions observed are (a) $^4\text{I}_{15/2} \rightarrow ^2\text{G}_{11/2}$ (376 nm), (b) $^4\text{I}_{15/2} \rightarrow (^2\text{G}, ^4\text{F}, ^2\text{H})_{9/2}$ (405 nm), (c) $^4\text{I}_{15/2} \rightarrow (^4\text{F}_{5/2}, ^4\text{F}_{3/2})$ (450 nm), (d) $^4\text{I}_{15/2} \rightarrow ^4\text{F}_{7/2}$ (486.5 nm), (e) $^4\text{I}_{15/2} \rightarrow ^2\text{H}_{11/2}$ (hypersensitive transition, 522 nm), (f) $^4\text{I}_{15/2} \rightarrow ^4\text{S}_{3/2}$ (540 nm), (g) $^4\text{I}_{15/2} \rightarrow ^4\text{F}_{9/2}$ (650.5 nm) and (h) $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2}$ (974.5 nm, Figure 8, *right*) [66].

Figure 8. UV-Vis absorption spectra in 10^{-5} M methanol solution (*left*) and in 10^{-3} M methanol solution (*inset, left*); NIR absorption spectrum in KBr pellets (*right*).

3.6.2. Calculated absorption spectra

With a view to their practical applications, the ground state geometry of the molecule can be regarded *irrelevant*, while an accurate prediction of where the ligand-associated absorption occurs for these highly coordinated lanthanide complexes is crucial. Most popular ligands are UV-excitable [67], which can be unwanted and even harmful for living tissue, in the case of bio-sensing applications. Furthermore, no cheap pump sources are available in the UV [68]. Thus, one of the growing challenges in the chemistry of the lanthanide ions is to develop NIR luminescent lanthanide complexes that can be sensitized in the visible range (>400 nm) [69,70]. Consequently, the ability to predict at which wavelength can a complex be excited is deemed crucial, and computational chemistry tools that can reliably model and predict the absorption and luminescent properties hold great potential so as to speed-up this materials design process.

As far as we know, there are no TDDFT studies of the absorption spectra of coordination compounds with erbium. For this reason, we attempted a real-time TDDFT calculation of the optical absorption spectrum of $[\text{Er}(\text{acac})_3(\text{bath})]$ in vacuum.

Spectra comparison. Regarding the use of semi-empirical calculations, the predicted spectra obtained with the INDO/S method and the different optimized geometries are very similar to each other and resemble the experimental one, except for the extra peak at *ca.* 250 nm (Figure 9). The approximations are acceptable for practical purposes for all Hamiltonians, albeit they display a systematic blue shift, which has been reported to range between 10 and 30 nm [71]. Conversely, the maximum of the TDDFT spectrum is strongly red-shifted in comparison with the experimental. This can be due to the limitations of TDDFT calculations for charge-transfer systems, such as the

one under study. Although this is most likely the main reason behind the strong red-shift of the computed spectrum, the influence of the crystallographic environment cannot be neglected either. The calculations were done in the gas phase, albeit using the crystallographic geometry. Although technically not difficult, the optimization of the geometry of the full complex was not done, as it would lack physical meaning, since the absorption would then be computed for the gas phase geometry, while the experimental results were obtained for the bulk material. Not optimizing the geometry amounts to assuming that the main effect of the crystallographic environment of the complex on the absorption spectrum is the distortion of the complex geometry relative to the gas phase geometry. The impact of this possibly minute distortion can be assessed by comparing the spectra for the acetylacetonate ligand computed using the XRD geometry and for the optimized (gas phase) geometry (see Figure 10). This validates the assumption that the use of the unrelaxed geometry somehow mimics the main impact of the crystallographic environment. But the neglect of other effects, such as, e.g., environmental polarization, will certainly also contribute to the discrepancy between theoretical and experimental spectra.

Figure 9. Comparison between the experimental (*black line*) and computed spectra of $[\text{Er}(\text{acac})_3(\text{bath})]$, using semi-empirical methods (AM1, PM3, PM6 and PM7) and real-time TDDFT. The TDDFT spectrum was computed using compressed sensing techniques [49].

Figure 10. Absorption spectra for the acetylacetonate ligand using the XRD and the optimized (gas phase) geometries to assess the effect of the geometry optimization.

3.7. Excitation spectrum

The excitation spectrum (Figure 11) consists of a broad band (from 325 to 450 nm, with a maximum at ca. 378 nm), associated to the excitation of the organic chromophores, and weaker intraconfigurational $f-f$ transitions, from the $^4I_{15/2}$ ground state to the $^4F_{7/2}$ (486 nm) and $^2H_{11/2}$ (522 nm) levels of the Er^{3+} ion, in good agreement with the spectra reported by Ilmi *et al.* for analogous Sm(III) and Eu(III) complexes [65]. The excitation spectrum reveals that the energy transfer from the ligands to Er^{3+} center is efficient, since the ligand-mediated excitation band is dominant in comparison to the $f-f$ transitions.

Nonetheless, it is worth noting that there is a significant shift of ca. 100 nm between the maximum of UV-Vis absorption spectrum and that of the excitation spectrum. According to Ilmi *et al.* [65], aforementioned broad band in the excitation spectrum would correspond to the triplet state of the ligand. The presence of such a $\pi-\pi^*$ spin-forbidden transition has been documented in the literature for acetylacetonone [72]. According to Woo *et al.* [73], although absorption selection rules for photons forbid singlet-to-triplet transitions, it is known that, in the solid state, the excited states are not pure singlet or triplet states (and the excitation spectrum presented herein was collected in powder form). Furthermore, there is consensus on the presence of a triplet at that energy: Walzl *et al.* [74] reported that Hacac has a spin-forbidden transition beginning at 3.15 eV with a maximum at 3.57 eV, that can either be attributed to $\pi-\pi^*$ singlet-triplet ($S-T$) excitation in the acetylacetonone enol or possibly to a $\pi-\pi^*$ ($S-T$) excitation in the acetylacetonone keto form, very close to the 3.60 eV value reported by Nakanishi *et al.* [75] for the acetylacetonate anion. Moreover, using the complete active space self-consistent field (CASSCF) and density functional theory (DFT) methods (CAS(10,8) calculations), Chen *et al.* [76] determined the adiabatic excitation energy from $E-S_0$ to $E-T_2$ ($^3n-\pi^*$) to be 3.34 eV, very close to the 3.28 eV value obtained from the experimental data. For comparison purposes, the positions (not the intensities) of the triplets have also been calculated by semi-empirical methods (dashed lines in Figure 11), which display the systematic hypsochromic shift (vs. the experimental spectrum) found in this type of calculations [71].

Figure 11. Excitation spectrum (*solid line*) and wavenumbers of the calculated triplet states (*dashed lines*, with arbitrary intensities).

3.8. Photoluminescence in solid state

Because the molar absorption coefficients ϵ of most of the transitions in the absorption spectra of the trivalent lanthanide ions are smaller than $10 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$, only a very limited amount of radiation is absorbed by direct excitation in the $4f$ levels. Since the luminescence intensity is not only proportional to the luminescence quantum yield but also to the amount of light absorbed, weak light absorption results in weak luminescence. However, the problem of weak light absorption can be overcome by the so-called *antenna effect* (or sensitization) in which energy is transferred from the surroundings of the metal ion (i.e. from organic ligand via resonant energy transfer). In order to evidence the importance of this ligand sensitization effect, the emission spectra upon direct excitation of the Er^{3+} hypersensitive transition nearly 532 nm was also collected. The corresponding emission spectra (Figure 12) have been corrected for the different source intensities at 350 nm and at 532 nm. It can be observed that the shape of the spectrum is the same in both cases, but upon excitation at 532 nm the PL intensity is half or a third than that gained upon excitation at 350 nm.

Figure 12. Comparison between emission spectra with excitation at 350 nm and at 522 nm.

3.9. Lifetime measurements

The PL decay of the $^4\text{I}_{13/2}$ multiplet was measured after $^4\text{I}_{11/2}$ excitation (Figure 13). In spite of the possible PL reabsorption, the obtained decay shows single exponential behavior, with a time constant of $1.02 \mu\text{s}$. This value, typical of lanthanide complexes [13,70,77] (and far smaller than the emission decay time of the isolated ion, $\tau \approx 8 \text{ ms}$), is due to vibronic coupling with high energy C–H stretching vibrations in the neighbourhood of the Er^{3+} ion (originated from the ligands), which lead to quenching of the excited state (because of the relatively small energy gap between the excited state $^4\text{I}_{13/2}$ and the ground state). For comparison purposes, this lifetime value is five times larger than that reported for erbium(III) tris (8-hydroxyquinolate) or ErQ_3 ($0.2 \mu\text{s}$ in powder form) [47], but significantly smaller than those attained for $\text{Er}(\text{F-tpip})_3$ (where HF-tpip stands for tetrapentafluorophenylimidodiphosphinate) [78] or for perfluorinated nitrosopyrazolone-based erbium chelates [79]: $164 \mu\text{s}$ and $15.7 \mu\text{s}$, respectively.

Figure 13. 1540 nm emission time decay measurement

4. CONCLUSIONS

Taking the simplest β -diketone, acetylacetone (Hacac), and a bulky N,N-donor (bathophenanthroline) as coordinating ligands, we have synthesized and thoroughly characterized a novel octacoordinated Er(III) complex, $[\text{Er}(\text{acac})_3(\text{bath})]$. Subsequently, this data has been used as a reference in order to assess the *goodness* of several semi-empirical calculation methods for the modelling of its structure and spectroscopic properties. Further, a comparison with TDDFT results for the optical absorption spectrum has also been conducted.

From the experimental results we can conclude that the material shows efficient sensitization by *antenna effect*, leading to NIR emission at 1.53 μs from Er^{3+} ions upon ligand excitation in the UV, and good thermal stability.

With regard to the Sparkle/AM1, -PM3, -PM6 and -PM6 Hamiltonians evaluation, it can be inferred that PM7 Sparkle/PM7 not only provides higher accuracy than the other semi-empirical methods for the prediction of the ground state geometry, but also proves to be much faster. In relation the spectroscopic optical absorption spectrum estimation, the differences in the predicted spectra using the geometries optimized with the various Hamiltonians and the INDO/S method are small and can be regarded as an acceptable approximation for practical purposes in all cases. Consequently, Sparkle/PM7 can be deemed as a very promising tool for the design of novel Ln(III) complexes.

Conversely, the much more computationally-intensive TDDFT calculations have failed to deliver a reasonable approximation to the UV-Vis spectrum, most likely due to the limitations of these calculation for charge-transfer systems, such as the one under study.

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