



RESEARCH ARTICLE

AN INVESTIGATION OF SPIN-ORBIT COUPLING OF $[\text{Eu}(\text{NO}_3)_3(2\text{pb})_2]\cdot\text{CH}_3\text{COCH}_3$
COMPLEX

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ABSTRACT

In this study, Eu metal investigated from lanthanides. $[\text{Eu}(\text{NO}_3)_3(2\text{pb})_2]\cdot\text{CH}_3\text{COCH}_3$ (Trinitratdi-(2-pyridilbenzimidazol)Eu(III).Aseton) complex was structurally optimized by using the Gaussian program. Geometric structure, molecular geometry, optimized geometric parameters, bond length, and bond angle of the complex were calculated using the SDD basis set of (DFT/B3LYP). HOMO- LUMO gap energies were calculated using the DFT method. The spin-orbit coupling parameter of the complex was theoretically calculated. Magnetic susceptibility analysis was performed using this value.

Keywords: Eu complex, DFT, HOMO-LUMO, Spin-Orbit Coupling

1. INTRODUCTION

In the periodic table, the generic name of 14 elements in which the atomic numbers are between 57 and 71 are called lanthanides [1]. It is well known that the 4f electrons in these elements play a crucial role in the physical properties such as electrical conductivity, magnetic properties, and optical interactions [2]. Also, the complexes produced by lanthanides have a +3 valence state, and the ligands directly affect the physical and chemical properties. As an example, the color of the complexes having lanthanide ions changes with the change of the ligands in the complexes [3].

The best-known application of the lanthanide complexes is the optical application such as LED and laser-based devices since they have a narrow bandgap, which gives a single color in the spectra. Besides this, the magnetic properties of the lanthanides do not show Curie-Weiss type behavior since the magnetic properties strongly depend on the angular momentum [4]. It is well known that the magnetization is explained by the sum of the spin angular momentum and the orbital angular momentum. When we consider the electron spin configuration of Lanthanides, it is seen that there is no contribution to the magnetization since it is zero [5]. So it is crucial to the determination of the spin-orbit coupling parameters which is related to the angular momentum of the complexes. For this purpose, we focused on the Eu complexes to investigate the magnetic interactions [6].

Europium is the element with the lowest melting point and lowest density among the lanthanides. It is also the most reactive metal in its group [7]. The most common use of Europium is related to phosphorescence property. It is well known that the electrons in the phosphorescent materials didn't immediately return the ground state when they excited [8].

The magnetic interactions in the lanthanides complexes take the attention of the scientist since they have unique properties such as high angular momentum contribution when compared to the transition

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metal complexes [9]. Also, spin-orbit coupling gives information about the interaction of magnetic dipole moment and orbital motion of the f-shell electrons for lanthanides, and these interactions have a crucial role for spintronic devices [10]. In this study, $[\text{Eu}(\text{NO}_3)_3 (2\text{pb})_2] \cdot \text{CH}_3\text{COCH}_3$ (Trinitratdi-(2-pyridilbenzimidazol)Eu(III).Aseton) complex was theoretically analyzed with the gaussian program. The magnetic interactions and spin-orbit coupling values of the complex and pure Eu^{+3} ions were calculated.

2. MATERIALS AND METHODS

$[\text{Eu}(\text{NO}_3)_3 (2\text{pb})_2] \cdot \text{CH}_3\text{COCH}_3$ molecule was used for theoretical study in the Gaussian program. During to design of the molecule, Eu^{+3} ions were settled at the center of the complex. Figure 1 shows the drawing of the complex in the GaussView 5.0. The geometrical optimization of the complex was performed in the Gaussian 09W program using the B3LYP (Becke, three parameters, Lee-Yang-Parr) / SDD base set in the DFT calculation. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) calculations of the complex, whose geometric optimization is completed, were obtained. The energy difference between the two values was determined. The information of the spin-orbit coupling parameters of the Eu-complex was seen in the study of [11], and it was developed a program for the calculation using the LabVIEW 2017 program in the Piri Reis Research Center of the Faculty of Arts and Sciences of İnönü University. The obtained spin-orbit coupling values for Eu^{+3} ions and $[\text{Eu}(\text{NO}_3)_3 (2\text{pb})_2] \cdot \text{CH}_3\text{COCH}_3$ complex was obtained.

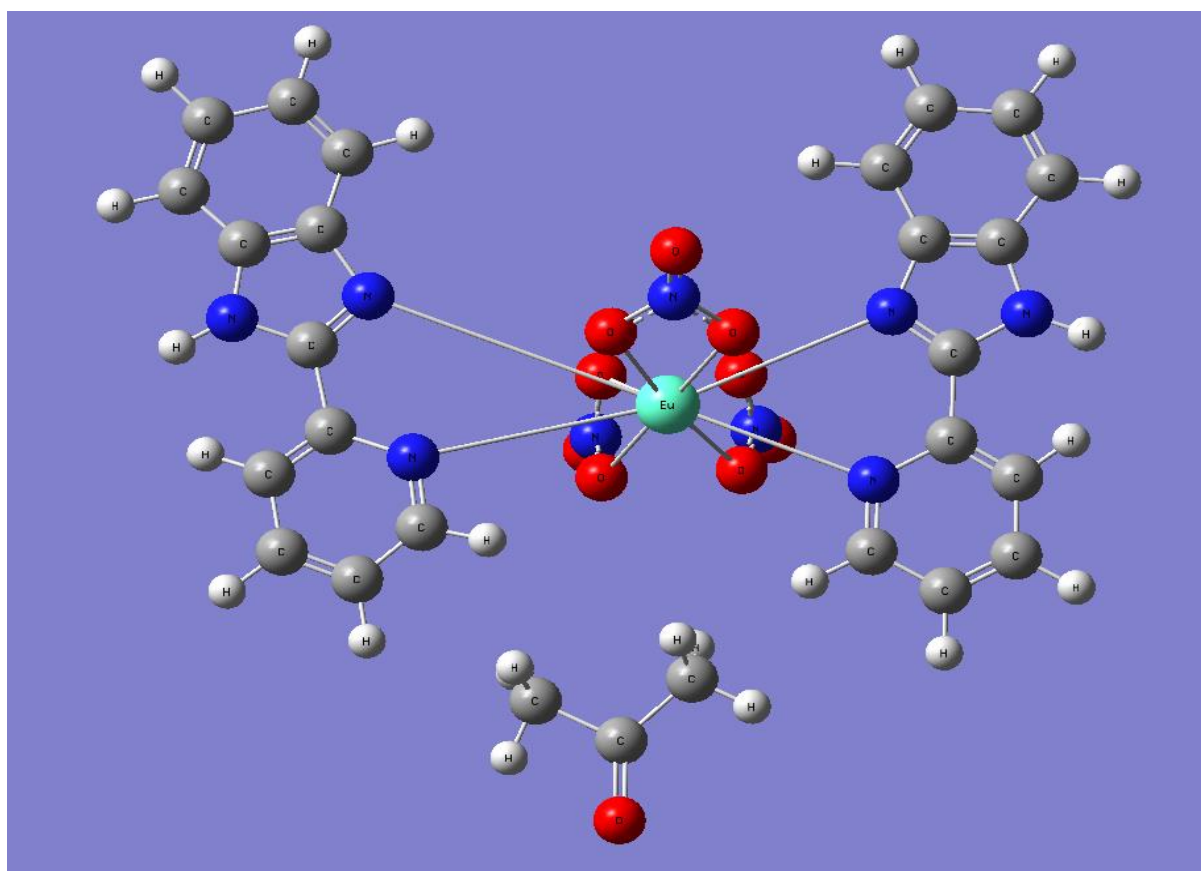


Figure 1. $[\text{Eu}(\text{NO}_3)_3 (2\text{pb})_2] \cdot \text{CH}_3\text{COCH}_3$ molecular structure in GaussView

3. RESULTS AND DISCUSSION

Figure 2 shows the structure of $[\text{Eu}(\text{NO}_3)_3 (2 \text{ pb})_2] \cdot \text{CH}_3\text{COCH}_3$ after geometric optimization in the Gaussian program. It is seen that the Figure 1 and 2 exhibits the effect of the DFT calculation in the structure. After optimization, we presented the bond lengths in the complex as given in Table 1. In the table, the donor atoms connected from ligand to the central atom and have a valid place in the formation of the complex. It is well known that the donor atoms give a part of the electron density in the opposite direction. Therefore, the relationship between the central atom and the donor atoms is investigated [12-13].

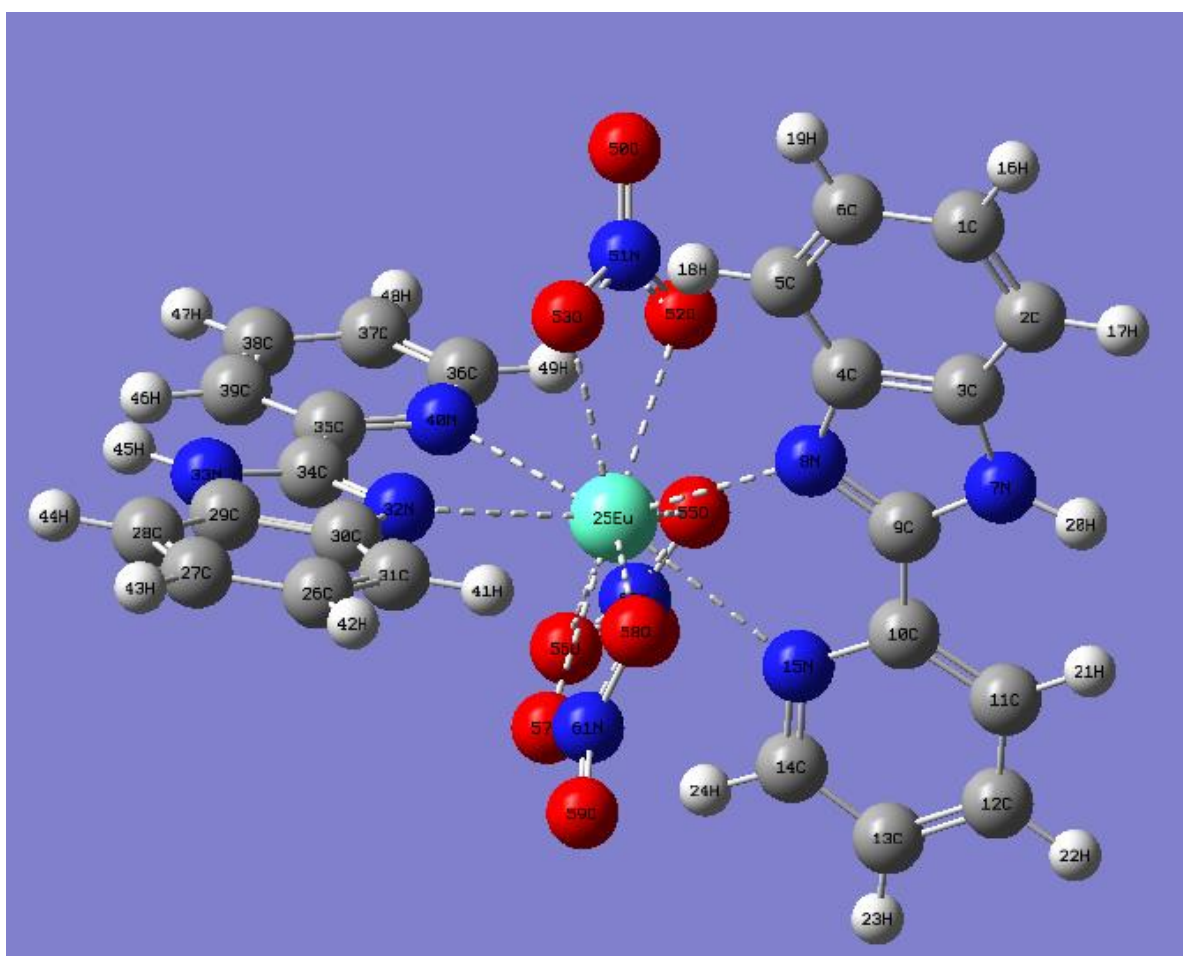


Figure 2. Geometrical optimization of $[\text{Eu}(\text{NO}_3)_3 (2 \text{ pb})_2] \cdot \text{CH}_3\text{COCH}_3$ the complex

Table1. Bond angles and bond lengths in the complex as a result of DFT calculations

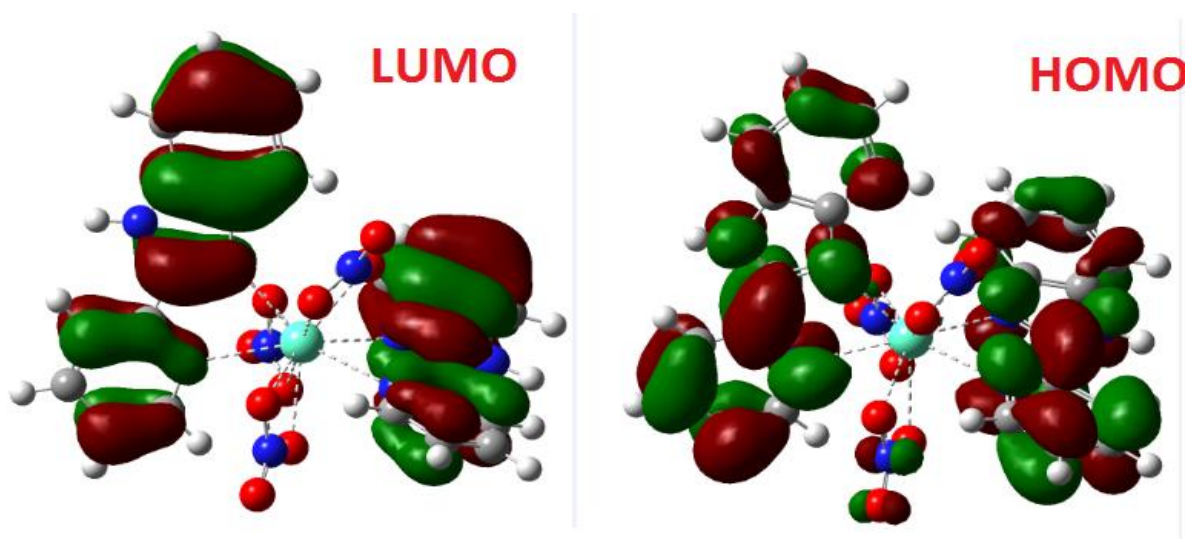
Complex	Bond Lengths (Å)
Eu25 – O52	2.580
Eu25 – O53	2.534
Eu25 – O55	2.566
Eu25 – O56	2.567
Eu25 – O57	2.581
Eu25 – O58	2.534
Eu25 – N8	2.670
Eu25 – N15	2.716
Eu25 – N32	2.669
Eu25 – N40	2.717
N8 – C4	1.393
N8 – C9	1.330
N15 – C10	1.352
N15 – C14	1.342
N32 – C30	1.393
N32 – C34	1.330
N40 – O35	1.352
N40 – C36	1.341
Angle	
O55 - Eu25 – O56	43.89
O57 - Eu25 – O58	50.11
O52 - Eu25 – O55	65.24
O52 - Eu25 – O53	50.11
O53 - Eu25 – N32	68.22
O58 - Eu25 – N8	68.24
O56 - Eu25 – N40	69.44
O58 - Eu25 – N15	71.46
O57 - Eu25 – N15	70.79
O58 - Eu25 – N32	77.04
N40 - Eu25 – N32	62.79
N8 - Eu25 – N15	62.80
O57 – 61N – O58	115.76
O55 – 60N – O56	115.56
C35 – 40N – C36	118.18
C30 – 32N – C34	105.70
C10 – N15 – C14	118.19
C4 - N8 – C9	105.70

The values given in Table 1 are the values obtained after geometric optimization. After the optimization with the Gaussian program, the coordinate states of the complex and the ligand significantly changed the symmetry of the molecular structure. If we analyze the bond lengths after optimization; The range of values of the bonds between the Eu central atom and the O donor atom is approximately 2.5604 (Å). Besides, the range of values of the bonds between the Eu central atom and the N donor atom is approximately 2.6930 (Å). Bond lengths between C-N atoms are also within a certain range of value. They have an average value of 1.3544 (Å), so these bonds are weaker than the others [14].

Table 2. Calculated HOMO, LUMO and E_g values of complex

Complex	HOMO, eV	LUMO, eV	E_g , eV
[Eu(NO ₃) ₃ (2 pb) ₂]·CH ₃ COCH ₃ 4.30185	-6.43931	- 2.13746	

The HOMO and LUMO energy levels of the complex and the E_g value, which is the difference between them, are given in the Table 2. The gap between HOMO and LUMO values is defined as the chemical stability of the molecule [15]. These values contain essential information about the electronic structure of the complex. Interactions are more comfortable as the energy difference between HOMO and LUMO decreases. Many physical and chemical quantities such as electron affinity, ionization potential, electronegativity, chemical hardness, and chemical softness can be calculated using HOMO and LUMO border orbital energies [16]. The HOMO and LUMO energy orbitals of the complex are shown in Figure 3.

**Figure 3.** Optimized molecular structure, HOMO and LUMO of complex

To determine the magnetic properties of the Eu⁺³ ion, we performed the magnetic moment and magnetic susceptibility analysis of these ions [17]. For this purpose, magnetic data and detailed numerical data of Eu(NO₃)₃(2pb)₂]CH₃COCH₃ complex and Eu⁺³ ion are given in Table 3.

Table 3 Theoretical value of Eu⁺³ and experimental μ_{eff} value of the complex and calculated spin-orbit parameters (λ_{LS})

Complex	μ_{eff} (μB)	Reference	λ_{LS} (cm^{-1})
[Eu(NO ₃) ₃ (2pb) ₂]·CH ₃ COCH ₃	3,480	18	1771,20
Eu ⁺³	3,508	17	1561,44

When we compare the spin-orbit coupling parameters, we saw that μ_{eff} value has an inverse ratio with λ_{LS} , which is related to quantum mechanical calculation [18].

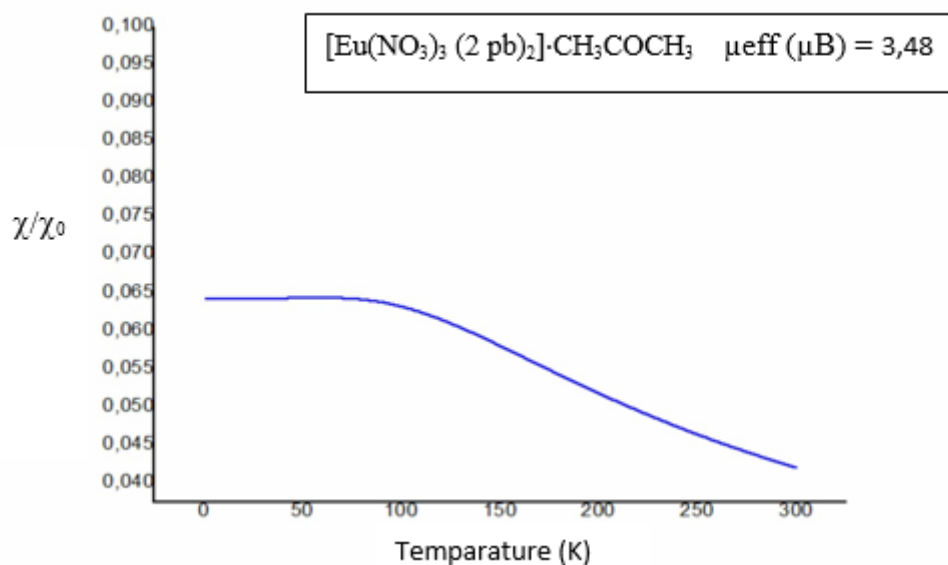


Figure 4. The magnetic susceptibility graph of the spin-orbit coupling value of the complex

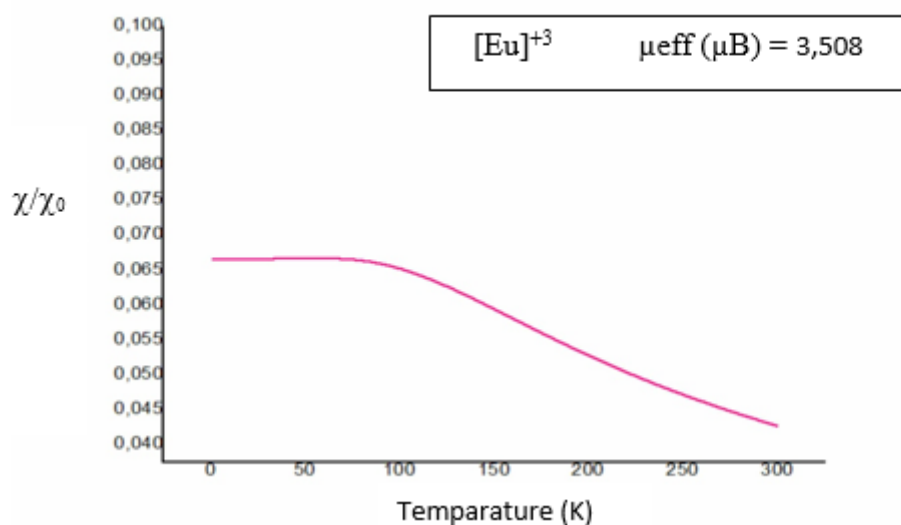


Figure 5. The magnetic susceptibility graph of the spin-orbit coupling value of the $[Eu]^{+3}$ ion

4. CONCLUSIONS

Geometric structure, molecular geometry, optimized geometric parameters, bond length, and bond angle quantum chemical calculations of $[Eu(NO_3)_3 (2 pb)_2] \cdot CH_3COCH_3$ complex were calculated using the SDD basis set of (DFT/B3LYP). HOMO-LUMO orbital energies were calculated using the DFT method. Besides, spin-orbit coupling values of the complex and the Eu^{+3} ion were compared. It is seen that spin-orbit interaction changes depending on the ligand around the central atom. The μ_{eff} value of the Eu^{+3} ion indicates that the presence of the ligand in the complex and spin-orbit coupling constant change. It is seen that theoretical calculations support experimental data. In addition, the bond length values of O donor atoms calculated as a result of the geometric optimization of the

complex are smaller than the bond length values of the N donor atoms. This is an expected result because weak field ligands have less electrostatic field.

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