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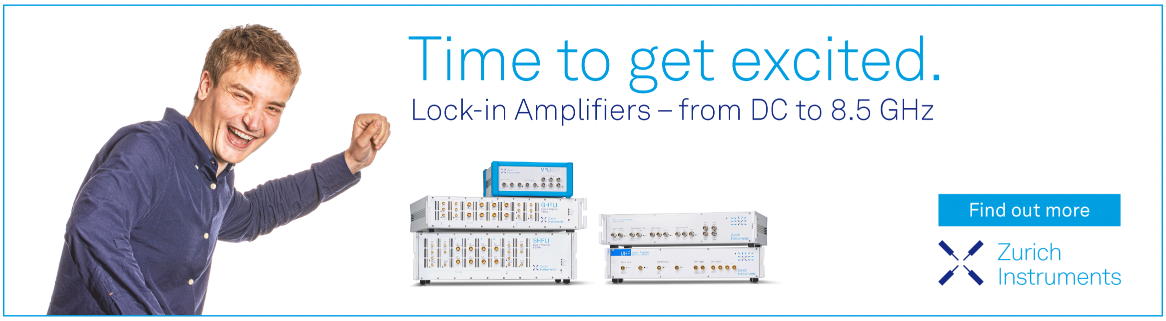

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Synthesis and interaction of adenosine-5'-triphosphate with rare earth metal europium (Eu^{3+})

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Abstract. Lanthanides and nucleotides can form attractive organic coordination polymers. Our study explore about the reaction of adenosine-5'-triphosphate (ATP) with europium(Eu^{3+}) and study its bonding characteristics through the FT-IR spectrum and UV-Vis spectroscopy. The results showed that the Eu(III) complex with adenosine-5'-triphosphate (ATP) was successfully synthesized and could interact in oxygen atoms from the phosphate group and nitrogen atoms from the adenine base with the highest absorption at the ATP:Eu^{3+} ratio of 1:2.

INTRODUCTION

Lanthanides have different magnetic, catalytic and optical properties based on specific 4f orbitals. The application of lanthanides has been more advanced than before, by enhancing their properties through synthesis with various ligands so that they can be used as contrast imaging materials, catalysts and biosensors [1]. Lanthanides are different from transition metals because they can bind to nitrogen bases and nucleotide phosphate groups. Nanoparticles formed by lanthanide bonds with phosphate groups are more important than nitrogen bases [2]. Tb^{3+}/GMP has formed intense green emissions that are seen in the water and this is related to the transfer of $^5D_4$ orbital energy from the metal Tb(III) to the GMP ligand. In other types of phosphate nucleotides, no fluorescence is observed that can support the interaction of Tb (III) with guanine used in energy transfer. These nanoparticles have been studied as protein encapsulation agents and dyes. The same application has been investigated with other types of lanthanide metals and AMP ligands [3].

Tan et.al have reported the Eu (III) nanoparticles which coordinate with AMP nucleotides and have similarities with other lanthanides [4]. However, it does not show fluorescence because the energy transfer is less than the state of the ligand excitation to the metal emission state. Nanoparticles become more hydrophobic and produce an increase in red fluorescence, through the addition of tetracycline as an "antenna" ligand and have overcome fluorescence deficiencies.

Nucleotides are excellent metal ligands, with nucleobases and phosphate groups for metal binding. Nishiyabu *et al*. has designed the first reported polymer coordination nanoparticle (CP) formed from various lanthanide (Ln) ions and purine nucleotides [5]. Under certain conditions, these materials can form hydrogels [6]. By using other metal ions, such as Zn^{2+} [7], Fe^{3+} [8], Au^{3+} [9-11], and Cu^{2+} [12], coordination materials that form hydrogels, coatings, and nanozym also has been displayed. Synthesis of lanthanide Tb^{3+} to nucleotide (AMP) as DNA adsorption material has also been carried out [13].

Lanthanides (Ln) can form nanoparticles with various nucleotides [14]. In a note from the Ministry of Energy and Mineral Resources (KESDM), Indonesia is estimated to have at least 1.5 billion tons of rare earth metals [18].

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Because of the abundance of rare earth metals, the superiority of lanthanide's unique properties that are easily applied to various fields and the formation of lanthanide complexes with nucleotide ligands has been investigated in various functions. Based on these advantages we have conducted the first study on lanthanide complexes, specifically the europium metal with ATP and studied the interaction of these complexes through spectroscopic studies.

EXPERIMENTAL

The Eu-ATP complex is synthesized based on previously reported methods [2]. The Adenosine-5'-triphosphate (ATP) solution (10 mM, 1 mL) was added to the $EuCl_3$ solution (5 mM, 1 mL) by mixing with stirring, and a white precipitate was formed immediately. After stirring for 2 hours at room temperature, the complex product is collected by centrifugation at 14,000 rpm for 10 minutes followed by washing three times with water and centrifugation. The complex compound is dried and analyzed by Shimadzu FT-IR spectrophotometer using KBr pallets. In comparison, europium metal and ATP ligand were also analyzed by FT-IR spectrophotometer. The ATP ligand stock solution made with a concentration of 0.005 mM reacts with the metal Eu (III) with a concentration from 0.00167 mM to 0.0175 mM with a molar ratio (3:1, 2:1, 1:1, 1:2, 1:3 and 1:3,5) for the measurement of UV-Vis absorption spectrum used in the determination of complex mole ratios.

RESULTS AND DISCUSSION

The FT-IR spectra of the Eu(III) metal complex, ATP and the Eu-ATP ligand were measured in the region of 150-4000 cm^{-1} and shown in Figure 1. The absorption bands of the Eu-ATP complex 3419 cm^{-1} show the OH group, Peak 2708 cm^{-1} and 2358 cm^{-1} in the ATP ligand showed that the C=N bond shifted to a peak of 2360 cm^{-1} indicating the possible coordination of nitrogen, N_1 and N_7 as donor electrons with the Eu^{3+}. The peak of 1712 cm^{-1} in the ATP ligand shifted to a strong peak in the area of 1639 cm^{-1} indicating deformation in the primary amine phase of NH_2 that occurred in the region of 1660-1590 cm^{-1}. This is in line with the Eu^{3+} bond attached to the nucleotide (AMP) where the shift from 1646 to 1600 cm^{-1} showed that the metal coordination bonds with AMP ligands through the bases of nitrogen and phosphate nucleotides [15].

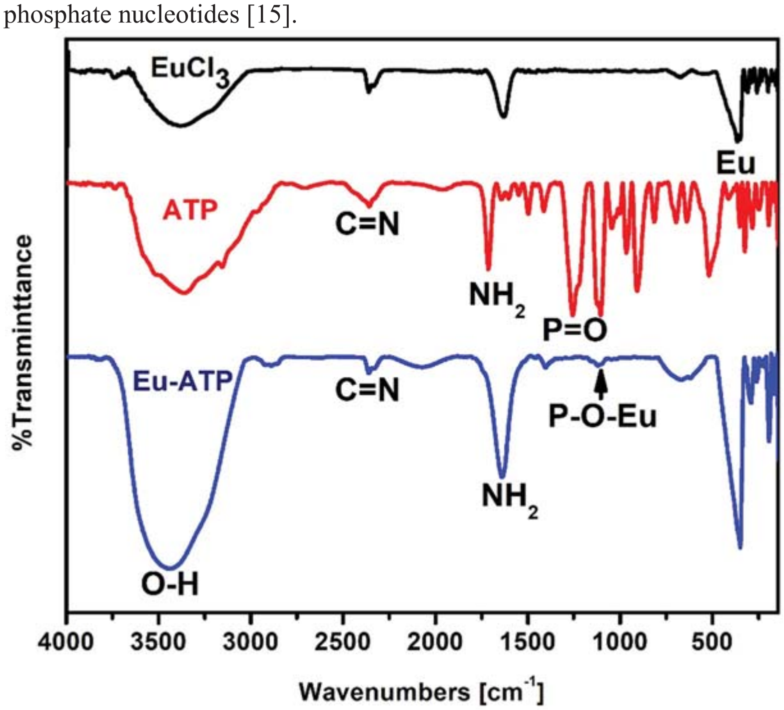

FIGURE 1. FT-IR spectrum of metal Eu(III), ATP ligand and Eu-ATP complex

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Two peaks of the ATP 1255 cm^{-1} and 1124 cm^{-1} ligands shifted at 1120 cm^{-1} in the Eu-ATP complex where stretching vibration P=O in the frequency region of 1350-1140 cm^{-1}, this shows the interaction of Eu(III) metals with oxygen atoms in phosphate groups as electron donors.

The peaks of 1001 cm^{-1}, 966 cm^{-1} and 908 cm^{-1} in ATP ligands indicate the presence of P-O-P bonds which are marked by a strong IR band at absorption between 1025-870 cm^{-1}. In the ATP ligand, there are strong peaks in the 638 cm^{-1} and 696 cm^{-1} areas which indicate the functional group of 8-monosubstitute purines in the 656-625 cm^{-1} area which merge into one with two peaks of 619 cm^{-1} and 671 cm^{-1} Fig. 1 shows the coordination of the metal bond Eu(III) to the adenine base ring. The absorption band in the region of 349 cm^{-1} is the Eu(III) metal fingerprint area seen in the Eu-ATP complex which shows the binding of Eu(III) metal with ATP [16].

The absorption spectrum of Eu(III) metal, ATP ligand, and Eu-ATP complex was measured by UV-Vis spectroscopy in the area λ = 185-700 nm can be seen in Figure 2. The absorption band of the maximum ATP ligand at the wavelength of 258.5 nm which means the replacement of electronic transitions $\pi \rightarrow \pi^*$. The Europium metal absorption band at a wavelength of 393.5 nm shows a transition of $^7F_0 \rightarrow {}^5L_6$ and at a wavelength of 409.5 nm, a transition of $^7F_1 \rightarrow {}^5L_6$ occurs. In the Eu-ATP spectrum the characteristic peaks of ATP ligands at 258.5 and 337 nm were not found, these results suggest that there is no free ATP in the coordinated polymer and ATP is bound to the metal Eu(III) through chemical coordination. . In the Eu-ATP complex spectrum there are two new absorption bands at wavelengths of 311 and 528.5 nm. The absorption peak at a wavelength of 528.5 nm indicates a $^7F_0 \rightarrow {}^5D_1$ transition, this supports the formation of the Eu-ATP complex [17].

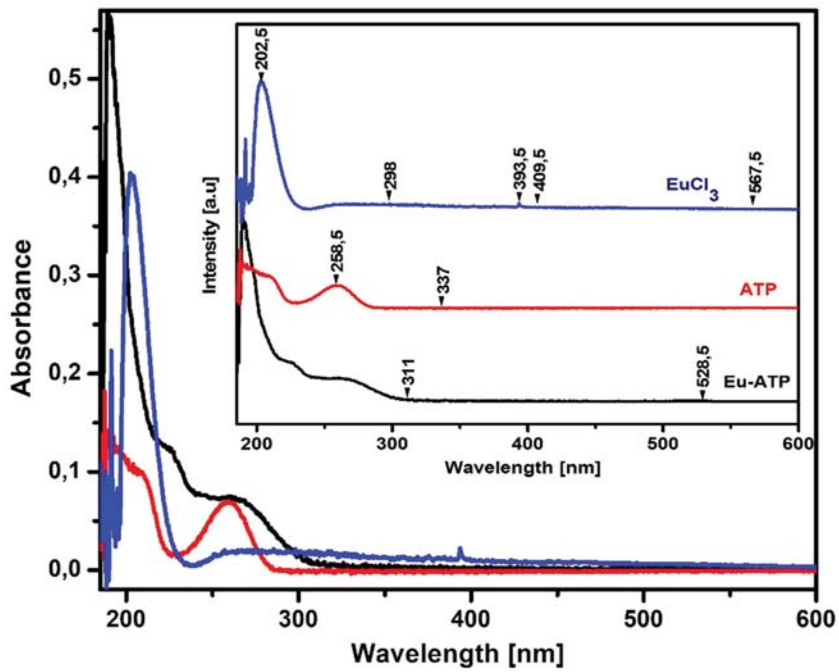

FIGURE 2. Absorption spectrum of Eu(III) metal, ATP ligand, and Eu-ATP complex was measured by UV-Vis spectroscopy in the area λ = 185-700 nm

Eu(III) metal stoichiometry bonding with ATP was observed through UV-Vis absorption spectrum of ATP 0.005 mM which reacted with Eu(III) metal at concentrations of 0.00167 mM to 0.0175 mM with molar ratios (3:1, 2:1, 1:1, 1:2, 1:3 and 1:3,5). The graph of the relationship between the metal moles of Eu(III) and the absorbance of Eu-ATP complex compounds can be seen in Figure 3. Absorbance increases with increasing number of moles of Eu(III) metal until it reaches the point of comparison of the ATP: Eu ratio of 1:2, then the absorbance decreases with the increasing number of moles of Eu(III) metal shows that there is no more number of Eu^{3+} bound ions. This proves that Eu^{3+} ions directly coordinate with nitrogen and oxygen atoms as electron donor atoms from the ATP nucleotide.

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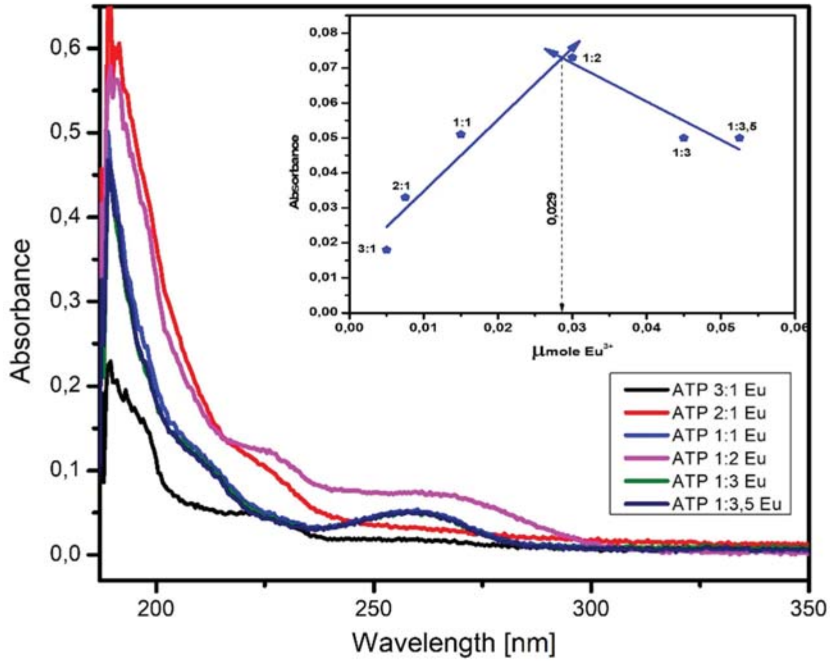

FIGURE 3. Absorbance spectrum at various mole ratios. Absorbance graph insert Vs micromol Eu^{3+}

CONCLUSION

Synthesis of metal Eu(III) with ATP ligand shows that complex compounds in the form of white powder have been successfully isolated and characterized, which shows the interaction of metal Eu(III) with ATP can occur through the coordination of nitrogen atoms from adenine. base atoms and oxygen from the ATP group the phosphate group as an electron donor group. The maximum absorption band of the ATP ligand at a wavelength of 258.5 nm which shows the electronic transition $\pi \rightarrow \pi$ *. In the absorption spectrum of the Eu-ATP complex the characteristic peaks of ATP ligands at 258.5 and 337 nm were not found, this result shows that ATP is bound to the metal Eu(III) and there are two new absorption bands at wavelengths of 311 and 528.5 nm. The absorption peak at a wavelength of 528.5 nm indicates an electronic transition of ${}^7F_0 \rightarrow {}^5D_1$ with an ATP: Eu ratio of 1:2, this supports that the Eu-ATP complex has been formed.

ACKNOWLEDGMENTS

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EXPLANATION STATEMENT and RESULT OF REVISED PAPER FROM REVIEWER

The highest thanks to reviewer who have patiently and meticulously read and revised the article we submitted previously titled : Synthesis and Interaction of Adenosine-5'-Triphosphate With Rare Earth Metal Europium (Eu^{3+}). With receipt number seri : 528_FP.

Representing other authors, I am very happy to receive your comment that you have presented in our article. We realize there are many shortcomings in our article so based on your directions, finally we can improve our article with some adjustments and revisions which also make us learn a lot from you. Some revisions and adjustments based questions :

No	Reviewer	Content	Page	Problem	Revised	Page
1.	No name	Introduction	1	At the end of this section, author say will use as biosensor. But the paper did not discuss the biosensor measurement? Please you confirm this part What kind the biosensor will apply?	We have synthesized europium metal with ATP and studied interactions as the first step for our next research, which this material will be used as a biosensor, but in this article we have not discussed it. We have fixed the last part of our introduction as follows: "Because of the abundance of rare earth metals, the superiority of lanthanide's unique properties that are easily applied to various fields and the formation of lanthanide complexes with nucleotide ligands has been investigated in various functions. Based on these advantages we have conducted the first study on lanthanide complexes, specifically the europium metal with ATP and studied the interaction of these complexes through spectroscopic studies".	1
2.	No Name	Material and Methods	2	Please revise your synthesis procedure step by step. How many do samples have produce?	we have explained in material and methods especially in the Preparation of Eu-ATP Synthesis section	2

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				Please explain properly		
3.	No Name	Result and Discussion	3	Fig 1. It should require some reference that confirm that the samples are successfully produce. Fig 2 and 3. Please enhance the quality of the Fig 2 and Fig 3 properly. The resolution at least 600 pixels.	We have added references that support the data in Figure 1. T. Hongliang, 2012 has synthesized Eu^{3+} with AMP and from the results of FT-IR analysis, nucleobase and phosphate groups play a role in bond formation. This is also similar to the ATP ligand we use where the metal is bound to the nucleobase and phosphate ligand group, and there is a change in the fingerprint area of the Eu(III) metal, and the white precipitate is formed from a synthesis process which reinforces that our compound has been successfully synthesized. Resolution of Fig 2 and Fig 3 has been improved	2 3-4
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