A tetranuclear lanthanide complex: structural, thermodynamic and vibrational properties

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Introduction

Complexes with multiple metal centers have interesting luminescence properties. Lanthanide complexes with four centers have been studied. For example, a lanthanide tetranuclear complex with two dysprosium(III), one europium(III) and one terbium(III) centers, when exposed to UV light, emitted blue light[1]. Here we have as our main objective the study of thermodynamic, structural and vibrational properties of the synthesis of a heterotrimetallic lanthanide complex by the Sparkle models[2].

Results and Discussion

Figure 1 shows the synthetic route of the heterotrimetallic lanthanide complex studied in this work.

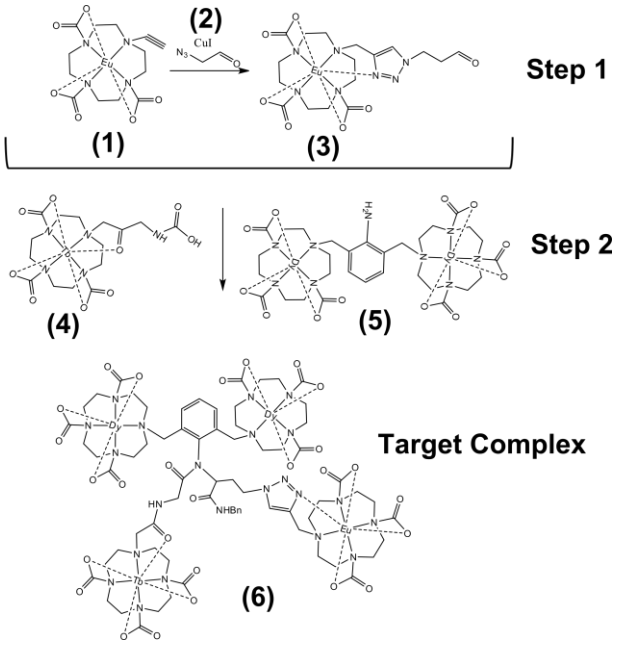

Figure 1. Synthesis of the heterotrimetallic lanthanide complex.

Initially, we optimized the geometries of the six species involved in the synthesis of the target complex, and no imaginary frequencies were obtained, thus indicating that all geometries are energy minima points of the potential energy surface. Tables 1 and 2 present the values of the enthalpies of formation of all six species involved in the synthesis of the target complex as well as the enthalpies of reaction of the two steps involved.

Table 1. Enthalpy of formation (in kcal.mol^{-1}) of the molecules involved in the synthesis of the heterotrimetallic lanthanide complex.

Complex/ Reagent	RM1	AM1	PM3	PM6
(1)	38	40	38	41
(2)	35	-1007	-1073	-113
(3)	22	-997	-1094	-144
(4)	-475	-2257	-2365	-378
(5)	-354	-1196	-1279	-283
(6)	-782	-4663	-4664	-775

Table 2. Enthalpy of reaction (in kcal.mol^{-1}) of the two steps involved in the synthesis of the heterotrimetallic lanthanide complex.

Step	RM1	AM1	PM3	PM6
1	-52	-30	-58	-72
2	25	87	74	30

We observed that all employed methods (RM1, AM1, PM3 and PM6) agree that the first step is probably thermodynamically favorable and the second step is not favorable.

Conclusion

All the geometries of the species involved in the synthesis of the target complex were optimized. No imaginary frequencies were found. The calculated enthalpies of reaction indicated that only the first step of the synthesis is energetically favorable.

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[2] Filho, M. a. M.; Dutra, J. D. L.; Rocha, G. B.; Freire, R. O.; Simas, *RSC Adv.***2013**, *3*, 16747.