

## Syntheses of europium complexes: ligand displacement order, inversion or retention of configuration, and reaction pathways via RM1 orbital model for lanthanides

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### INTRODUCTION

We show that the thermodynamic properties calculated for chemical reactions involving lanthanide complexes with the recently introduced RM1 orbital model for lanthanides are consistent with established experimental results involving europium complexes. Subsequently, we use this model for the elucidation of synthetic pathways aiming at the design of new and more efficient synthetic routes for mixed ligand luminescent europium complexes<sup>2</sup>.

### METHODS

All calculations were carried out in a version of MOPAC we modified to include the RM1 orbital model for lanthanides. The RM1 orbital model for lanthanides does not treat them as sparkles. For europium, it assumes that the neutral atom is represented by  $\{[\text{Xe}]4f^6\}6s^25d^16p^0$  with a semiempirical basis set comprised of 5d, 6s and 6p orbitals, introduced to allow a degree of covalency to occur between the ligands and the europium ion. The semiempirical core stands for  $\{[\text{Xe}]4f^6\}$  and corresponds to the core of the trication.

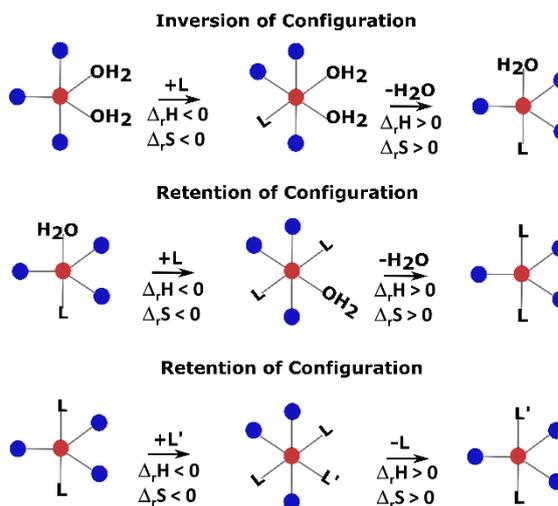
Calculations of enthalpy and entropy were carried out by using standard MOPAC algorithms.

Syntheses were carried out according to the methodologies we developed<sup>2</sup>.

### RESULTS AND DISCUSSION

Syntheses of mixed ligand luminescent europium complexes involve a number of displacement reactions of a nonionic ligand by another, each one leading to either a retention or inversion of configuration. The europium complexes calculated were all of the form  $\text{Eu}(\beta\text{-diketonate})_3(\text{L},\text{L}')$ , where the  $\beta$ -diketonates were DBM, TTA, and BTFA; and L and L' were TPPO, PTSO, DBSO, and H<sub>2</sub>O. Accordingly, we calculated the variation of enthalpy and entropy of all imaginable reactions of displacements of L by L', with both products and reagents in either cis or trans configurations. We then simulated the complete stepwise reaction pathways for ligand exchange. Results were in exact agreement with the displacement capability

of nonionic ligands with respect to each other, we also determined experimentally: TPPO > PTSO > DBSO > H<sub>2</sub>O. The calculations likewise accurately reproduced the observed inversion of configuration in the synthesis of  $\text{trans-Eu}(\beta\text{-diketonate})_3(\text{L})_2$ , from  $\text{cis-Eu}(\beta\text{-diketonate})_3(\text{H}_2\text{O})_2$ . Finally, calculations predicted the retention of configuration in the synthesis of  $\text{trans-Eu}(\beta\text{-diketonate})_3(\text{L},\text{L}')$  from  $\text{trans-Eu}(\beta\text{-diketonate})_3(\text{L})_2$ , (Fig. 1).



**Figure 1.** Predicted and already partially confirmed stepwise reaction pathways in the synthesis of  $\text{Eu}(\beta\text{-diketonate})_3(\text{L},\text{L}')$ .

### CONCLUSIONS

Our results indicate that the thermodynamic properties calculated via RM1 orbital model for europium have predictive value and can be useful for the design of new synthetic routes of mixed ligand luminescent europium complexes involving ligand displacement reactions.

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<sup>1</sup> Filho, M. A. M. et al. *J. Chem. Theory Comput.* 10, 3031–3037 (2014).

<sup>2</sup> Lima, N. B. D. et al. *Sci. Rep.* 3, 2395 (2013).