Theoretical thermodynamics of the synthesis of $Eu(TTA)_3(RSOR,TPPO)$ complexes by substitution reactions

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Introduction

Luminescent europium β-diketonate complexes are used in various important applications, such as in MOF's[1] as pH sensors[2]. The asymmetry of mixed europium complexes Eu(β-diketonate)$_3$(L,L'), leads to the intensification of the quantum yield and emission efficiency quantities when compared with what would be expected for the complexes with repeating ligands Eu(β-diketonate)$_3$(L)$_2$ and Eu(β-diketonate)$_3$(L')$_2$. In this work we performed Sparkle/AM1[3] calculations of displacement reactions of the type $Eu(TTA)_3(RSOR)_2$+TPPO→ $Eu(TTA)_3$(RSOR,TPPO) + RSOR, as well as $Eu(TTA)_3(TPPO)_2$ + RSOR→$Eu(TTA)_3$(RSOR, TPPO) + TPPO with RSOR being DBSO, PMSO, DPSO and PTSO. The molecular structures of the ligands are shown in Figure 1.

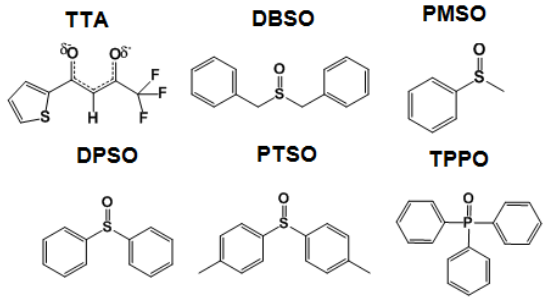

Figure 1. Molecular structures of the ligands considered in this work.

Results and Discussion

All calculations were carried out for the isolated molecules with the Sparkle/AM1 available in MOPAC 2012. The geometries were fully optimized in all cases and correspond to true energy minima as verified by the absence of imaginary vibrational frequencies by a subsequent force constant calculation, which are necessary for the calculation of the thermodynamic quantities. Table 1 shows all calculated thermodynamic quantities for the possible displacement reactions of the type $Eu(TTA)_3(RSOR)_2$ + TPPO → $Eu(TTA)_3$(RSOR,TPPO) + RSOR, as well as $Eu(TTA)_3(TPPO)_2$ + RSOR → $Eu(TTA)_3$(RSOR, TPPO) + TPPO.

Synthesis of $Eu(TTA)_3(L,L')$ complexes:

$Eu(TTA)_3(DBSO)_2$+ TPPO → $Eu(TTA)_3$(DBSO,TPPO) + DBSO
ΔHr=-16.9 kcal/mol, ΔGr=-8.8 kcal/mol
$Eu(TTA)_3(TPPO)_2$+ DBSO → $Eu(DBM)_3$(DBSO,TPPO) + TPPO
ΔHr= +17.4 kcal/mol, ΔGr= +9.0 kcal/mol

$Eu(TTA)_3(DPSO)_2$+ TPPO → $Eu(TTA)_3$(DPSO,TPPO) + DPSO
ΔHr=-15.6 kcal/mol, ΔGr=-0.9 kcal/mol
$Eu(TTA)_3(TPPO)_2$+ DPSO → $Eu(TTA)_3$(DPSO,TPPO) + TPPO
ΔHr= +23.4 kcal/mol, ΔGr=+5.1 kcal/mol

$Eu(TTA)_3(PMSO)_2$+ TPPO → $Eu(TTA)_3$(PMSO,TPPO) + PMSO
ΔHr=+5.0 kcal/mol, ΔGr=+31.5kcal/mol
$Eu(TTA)_3(TPPO)_2$+ PMSO → $Eu(TTA)_3$(PMSO,TPPO) + TPPO
ΔHr= +39.2 kcal/mol, ΔGr=+39.5 kcal/mol

$Eu(TTA)_3(PTSO)_2$+ TPPO → $Eu(TTA)_3$(PTSO,TPPO) + DPSO
ΔHr=-38.0 kcal/mol, ΔGr=-22.4 kcal/mol
$Eu(TTA)_3(TPPO)_2$+ PTSO → $Eu(TTA)_3$(PTSO,TPPO) + TPPO
ΔHr= 0.0 kcal/mol, ΔGr=-31.6 kcal/mol

Figure 2. Sparkle/AM1 thermodynamic data for the theoretical possibilities of displacement reactions for the preparation of $Eu(TTA)_3$(RSOR,TPPO) complexes from $Eu(TTA)_3(RSOR)_2$ or $Eu(TTA)_3(TPPO)_2$ complexes.

In all cases the TPPO ligand was capable of displacing the sulfoxide ligands since the enthalpies and Gibbs free energies of the reaction $Eu(TTA)_3(RSOR)_2$ + TPPO → $Eu(TTA)_3$(RSOR,TPPO) + RSOR are lower than the corresponding reactions $Eu(TTA)_3(TPPO)_2$ + RSOR → $Eu(TTA)_3$(RSOR, TPPO) + RSOR.

Conclusion

In conclusion, the enthalpies and Gibbs free energies of the reactions, calculated by the semiempirical Sparkle/AM1 model show that the reaction $Eu(TTA)_3(RSOR)_2$ + TPPO → $Eu(TTA)_3$(RSOR,TPPO) + RSOR, is predicted to be more likely to occur.

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