A theoretical study of the molecular properties of $Sm(L)_nCl_3$ complexes

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Keywords: *sparkle model, samarium, TPPO*

Introduction

Luminescent lanthanide complexes are used in several applications, such as functioning as markers which can selectively stain the nucleolus of determinate cells[1]. In this work we performed calculations, using the semiempirical RM1[2] method, of the structural, thermodynamic and vibrational properties of samarium trichloride complexes, $SmCl_3$, coordinated with the nonionic ligands DBSO, DPSO, PTSO and TPPO (see Figure 1), in different stoichiometric ratios $SmCl_3$: nL, n= 1 to 4.

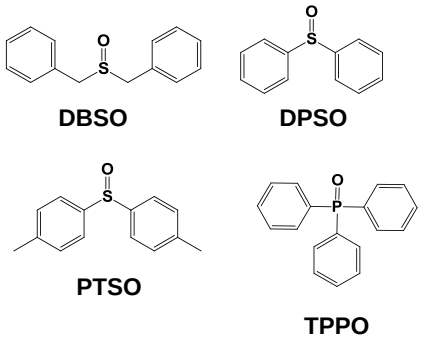

Figure 1. Molecular structures of the nonionic ligands DBSO, DPSO, PTSO and TPPO.

Results and Discussion

First, we calculated the fully optimized geometries of the complexes $Sm(L)_nCl_3$ with n ranging from 1 to 4. The nonionic ligands L were the phosphoxide compound TPPO and the sulfoxide compounds: DBSO, DPSO and PTSO. No imaginary frequencies were observed, indicating that the geometries correspond to minima in the potential energy surface. The calculations of the vibrational modes are also important to obtain the thermodynamic quantities. Table 1 shows the distances of the ligands to the samarium ion, δr O---Sm, and the main changes observed in the groups involved in coordination polyhedra. Our results show that the distances are around 2.28 Å for all complexes considered. Also, the S=O bonds increase by 0.199 Å and the P=O bonds by 0.101 Å upon complexation. The enthalpies of formation, ΔH_f, show that, for the complexes with sulfoxide ligands, the most stable one always possess three ligands. On the other hand, for the samarium complexes with the TPPO ligand, the most stable one possesses four nonionic ligands.

Table 1. Values of the distance of the nonionic ligand to samarium, the main observed changes in structural properties ($\Delta\delta r = \delta r^{Y=O}$ (in complex) - $\delta r^{Y=O}$ (free ligand), and the enthalpies of formation (ΔHf).

Samarium complex	δr O---Sm (Å)	ΔδrY=O (Å)	ΔH_f (kcal/mol)
$Sm(Cl)_3(DBSO)_1$	2.280	0.199	-87
$Sm(Cl)_3(DBSO)_2$	2.281	0.198	-106
$Sm(Cl)_3(DBSO)_3$	**2.281**	**0.198**	**-122**
$Sm(Cl)_3(DBSO)_4$	2.286	0.198	-115
$Sm(Cl)_3(DPSO)_1$	2.280	0.207	-79
$Sm(Cl)_3(DPSO)_2$	2.281	0,206	-89
$Sm(Cl)_3(DPSO)_3$	**2.281**	**0.206**	**-95**
$Sm(Cl)_3(DPSO)_4$	2.284	0.207	-83
$Sm(Cl)_3(PTSO)_1$	2.280	0.208	-98
$Sm(Cl)_3(PTSO)_2$	2.282	0.207	-127
$Sm(Cl)_3(PTSO)_3$	**2.282**	**0.206**	**-151**
$Sm(Cl)_3(PTSO)_4$	2.287	0.206	-148
$Sm(Cl)_3(TPPO)_1$	2.281	0.103	-132
$Sm(Cl)_3(TPPO)_2$	2.283	0.103	-185
$Sm(Cl)_3(TPPO)_3$	2.281	0.101	-232
$Sm(Cl)_3(TPPO)_4$	**2.287**	**0.101**	**-243**

Conclusion

In this work we performed semiempirical RM1 calculations to obtain data of structural and thermodynamic quantities. Our results show that, for the complexes involving sulfoxide ligands, the optimum number of nonionic ligands is three and for the complexes involving the TPPO ligand the optimum number is four.

Acknowledgments

CNPq,, PRONEX/FACEPE, PROAES/UFPE.

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