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Theoretical and experimental study of lanthanide ion complexes: Spectroscopy and chemical bond analysis

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Abstract: The theoretical intensity parameters of 4f-4f transitions in lanthanide complexes depend on the chemical environment and the nature of rare-earth ion, where in the absence of inversion center, the two main contributions are the forced electric dipole mechanism (FED) and the dynamics coupling (DC) mechanism [1,2]. The overlap polarizability (α_{op}) and ionic specific valence were recently used [3] to reshape and reinterpret the expressions of these two mechanisms, in which the ligand effective polarizability describes the environment polarizability not accounted into α_{op} . In this work, a set of different complex were analyzed by using the new methodology [3]. The investigated complexes are $[\text{Ln}(\beta\text{D})_3(\text{L})_X]$, (where $\text{Ln} = \text{Eu}^{3+}$, Tb^{3+} and Gd^{3+}) with β -diketones ligands βD (BZAC = benzoylacetonate; DBM = dibenzoylmethanate and TTA = 2-thenoyltrifluoroacetate) and ligands L derived from 2-aminopyridine (2AP) and 2-aminoprimitidine (2APM), wherein $X = 1$ or 2. These compounds were synthesized, characterized and their quantum efficiency, radiative (A_{rad}) and nonradiative (A_{nrad}) emission coefficients, and intensity parameters Ω_2 and Ω_4 where experimentally obtained from spectroscopic data (Table 1).

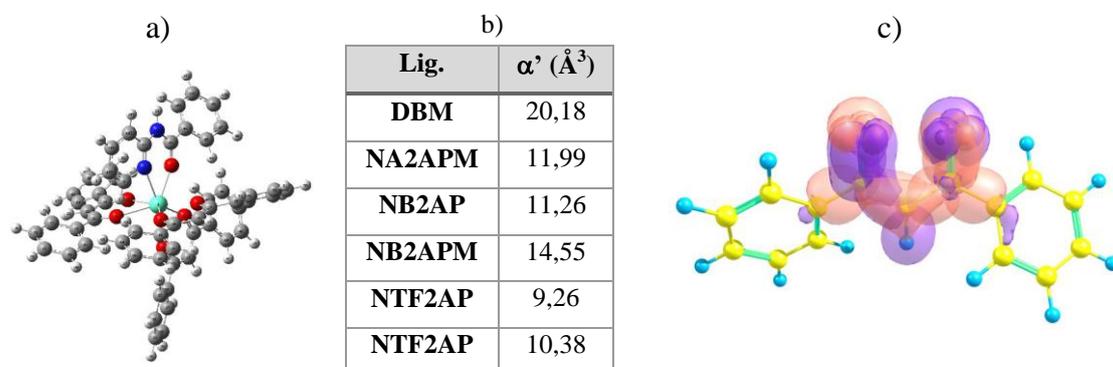


Figure 1. (a) Eu^{3+} complex $[\text{Eu}(\text{DBM})_3(\text{NP2AP})]$ (b) Table with the obtained values of the ligand effective polarizabilities; (c) DBM ligand orbitals localized at the coordination region.

It is known that the ligand field breaks the symmetry of the metal Ln, and modifies the electron density around the metal center. Consequently, the energies of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_\lambda$ transitions, on the Eu^{3+} ion (for example), also change as a consequence



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the nephelauxetic effect [1,2]. This electron density is dependent on the characteristics of the ligand, that is, whether a ligand is a soft or hard Lewis basis or if it has an electron donor or withdrawn substituent. The characterization of the $\text{Ln}^{3+}\text{-L}$ bond situation [2] reveals that chemically more polarizable bonds and environments contribute to increase of the intensity parameters in lanthanide compounds [1-3]. It can be seen in Table 1 that the experimental Ω_2 and Ω_4 values change a lot, when some systematic ligand modifications are imposed. For instance, Ω_2 for $[\text{Eu}(\text{DBM})_3(\text{NTF2AP})]$ is $18.6 \cdot 10^{-20} \text{cm}^{-2}$, while the same parameter for $[\text{Eu}(\text{DBM})_3(\text{NTF2APM})]$ is $37.3 \cdot 10^{-20} \text{cm}^{-2}$, making it clear the importance of the theoretical study.

Table 1. Experimental intensity parameters Ω_λ (in 10^{-20}cm^{-2}), radiative (A_{rad}), nonradiative (A_{nrad}) and total (A_{total}) emission coefficients (in s^{-1}), emitter lifetimes τ (in ms) and quantum efficiency η_{cal} (in %).

| Complexes | Ω_2 | Ω_4 | A_{rad} | A_{nrad} | A_{total} | τ | η_{cal} |
|--|------------|------------|------------------|-------------------|--------------------|--------|---------------------|
| $[\text{Eu}(\text{BZAC})_3(\text{H}_2\text{O})_2]$ | 16.9 | 2.2 | 437.7 | 4825.5 | 5263.2 | 0.19 | 8.3 |
| $[\text{Eu}(\text{BZAC})_3(\text{NA2APM})]$ | 21.9 | 2.5 | 541.5 | 582.1 | 1123.6 | 0.89 | 48.2 |
| $[\text{Eu}(\text{BZAC})_3(\text{NA2AP})]$ | 15.7 | 6.5 | 464.2 | 2984.1 | 3448.4 | 0.29 | 13.5 |
| $[\text{Eu}(\text{BTF})_3(\text{H}_2\text{O})_2]$ | 18.6 | 1.8 | 461.1 | 2170.5 | 2631.6 | 0.38 | 17.5 |
| $[\text{Eu}(\text{BTF})_3(\text{NTF2AP})]$ | 8.9 | 6.2 | 339.9 | 822.9 | 1162.8 | 0.86 | 29.2 |
| $[\text{Eu}(\text{BTF})_3(\text{NTF2APM})]$ | 18.4 | 2.5 | 466.8 | 723.7 | 1190.5 | 0.84 | 39.2 |
| $[\text{Eu}(\text{DBM})_3(\text{H}_2\text{O})_2]$ | 38.0 | 1.8 | 883.6 | 99116.4 | 100000 | 0.01 | 0.9 |
| $[\text{Eu}(\text{DBM})_3(\text{NTF2AP})]$ | 18.6 | 2.5 | 500 | 6167 | 6667 | 0.15 | 8.0 |
| $[\text{Eu}(\text{DBM})_3(\text{NTF2APM})]$ | 37.3 | 2.6 | 867.4 | 1513.5 | 2380.9 | 0.42 | 36.4 |
| $[\text{Eu}(\text{TTA})_3(\text{H}_2\text{O})_2]$ | 29.3 | 3.8 | 700.5 | 3466.2 | 4166.7 | 0.24 | 16.8 |
| $[\text{Eu}(\text{TTA})_3(\text{NA2AP})_2]$ | 29.1 | 2.5 | 688.7 | 1485.2 | 2173.9 | 0.46 | 31.7 |
| $[\text{Eu}(\text{TTA})_3(\text{NA2APM})_2]$ | 32.8 | 3.9 | 782.9 | 1103.9 | 1886.8 | 0.53 | 41.5 |
| $[\text{Eu}(\text{TTA})_3(\text{NTF2AP})]$ | 13.7 | 2.4 | 393.4 | 1035.2 | 1428.6 | 0.70 | 27.5 |
| $[\text{Eu}(\text{TTA})_3(\text{NTF2APM})_2]$ | 39.6 | 1.5 | 913 | 754 | 1667 | 0.6 | 55 |

Initial geometries of the complexes were pre-optimized by Sparkle/PM6 model, and were used as input for the DFT B3LYP/6-31+g(d) optimizations. The ligand effective polarizabilities were calculated using B3LYP/aug-cc-pVDZ methodology, where the α' values were calculated from the LMOs in a region within two bonds from the ligating oxygen atoms (Figure 1c). The Pipek-Mezey and Ruedenberg localization procedures were used. Each ligands geometries in all complexes were used to calculate the α' value, where some of the results are depicted in Figure 1b. It is important to highlight that the biggest calculated α' was obtained for the DBM ligand, which also has some of the biggest Ω_2 values. The recent developed JOYSpectra program has been used for the calculations of force constants, charge factors and theoretical intensity parameters.

Key-words: Spectroscopy; lanthanide ion; polarizability; chemical bond; DFT.

Support: UFPB, CAPES, CENAPAD/SP and LCCQS/UFPB.

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