

Structural Fluxionality of Luminescent Coordination Compounds with Lanthanide Ions

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Abstract : Complexes with lanthanide ions have been extensively studied due to their applications as luminescent, magnetic and catalytic materials as molecular or extended crystals, thin films, glasses, polymeric matrices, ionic liquids, and in solution. NMR chemical shift data in solution have been reported and suggest fluxional structures in a wide range of coordination compounds with rare earth ions. However, the fluxional mechanisms for these compounds are still not established. This structural fluxionality may affect the photophysical, catalytic and magnetic properties in solution. Thus, understanding the structural interconversion mechanisms may aid the design of coordination compounds with, for instance, improved (electro)luminescence, catalytic and magnetic behaviors. The [Eu(btfa)₃bipy] complex, where btfa= 4,4,4-trifluoro-1-phenyl-1,3-butanedionate and bipy= 2,2'-bipyridyl, has a well-defined X-ray crystallographic structure and preliminary ¹H NMR data suggested a structural fluxionality. Thus, we have investigated a series of coordination compounds with lanthanide ions [Ln(btfa)₃L], where Ln = La, Eu, Gd or Yb and L= bipy or phen (phen=1,10-phenanthroline) using a combined theoretical-experimental approach. These complexes were synthesized and fully characterized, and detailed NMR measurements were obtained. They were also studied by quantum chemical computational methods (DFT-PBE0). The aim was to determine the relevant factors in the structure of these compounds that favor or not the fluxional behavior. Measurements of the ¹H NMR signals at variable temperature in CD₂Cl₂ of the [Eu(btfa)₃L] complexes suggest that these compounds have a fluxional structure, because the crystal structure has non-equivalent btfa ligands that should lead to non-equivalent hydrogen atoms and thus to more signals in the NMR spectra than those obtained at room temperature, where all hydrogen atoms of the btfa ligands are equivalent, and phen ligand has an effective vertical symmetry plane. For the [Eu(btfa)₃bipy] complex, the broadening of the signals at -70°C provides a lower bound for the coalescence temperature, which indicates the energy barriers involved in the structural interconversion mechanisms are quite small. These barriers and, consequently, the coalescence temperature are dependent upon the radii of the lanthanide ion as well as to their paramagnetic effects. The PBE0 calculated structures are in very good agreement with the crystallographic data and, for the [Eu(btfa)₃bipy] complex, this method provided several distinct structures with almost the same energy. However, the energy barrier for structural interconversion via dissociative pathways were found to be quite high and could not explain the experimental observations. Whereas the pseudo-rotation pathways, involving the btfa and bipy ligands, have very small activation barriers, in excellent agreement with the NMR data. The results also showed an increase in the activation barrier along the lanthanide series due to the decrease of the ionic radii and consequent increase of the steric effects. TD-DFT calculations showed a dependence of the ligand donor state energy with different structures of the complex [Eu(btfa)₃phen], which can affect the energy transfer rates and the luminescence. The energy required to promote the structural fluxionality may also enhance the luminescence quenching in solution. These results can aid in the design of more luminescent compounds and more efficient devices.

Keywords : computational chemistry, lanthanide-based compounds, NMR, structural fluxionality

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