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Synthesis and characterization of three new *2p-3d-4f* heterotrispin complexes

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Molecular magnetic compounds with three different spin carriers are used as a strategy to obtain new magnetic materials meanwhile represent a challenge in the synthetic point of view.[1] The use of anisotropic ions in these systems can lead to compounds with properties of single-molecule magnets (SMMs), which are investigated due to their potential application in high density data storage devices and as spin quibts for quantum computing.[2] Nitronyl-nitroxide (NN) radicals are well-known paramagnetic building blocks used in the synthesis of new molecular magnetic materials and play a significant role in the formation of *2p-3d-4f* heterotrispin complexes.[3] A useful synthetic approach to obtain these heterotrispin systems is one-pot reaction using NN radicals substituted with additional coordination sites beyond nitroxide group to induce selective coordination to *3d* and *4f* metal ions based in hard-soft acid-base concept. In this work, we will present the synthesis, crystal structure, and investigation of magnetic properties of three new *2p-3d-4f* heterotrispin complexes with molecular formula [Ln(hfac)$_3${μ-(4-QnNIT)Cu(hfac)$_2$}$_2$], (Ln^{3+}= Gd, Tb or Dy for **1**, **2** and **3**, respectively) where *hfac*$^-$ is hexafluracetylacetonato and 4-QnNIT is 4-(quinoline)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide. The synthesis consists of a one-pot reaction by adding the 4-QnNIT radical to a boiling solution of the precursor complexes [Ln(hfac)$_3$(H$_2$O)$_2$] and [Cu(hfac)$_2$(H$_2$O)$_2$]. Suitable single crystal for X-ray diffraction experiments were obtained and the structures were determined. The three compounds are isostructural and consist of a lanthanide(III) ion coordinated by six oxygen atoms from three bidentate *hfac-* ligands and the other two positions are occupied by oxygen atom from nitroxide moiety of two 4-QnNIT radicals (Figure 1). Two 4-QnNIT radicals are bridging ligand connecting the lanthanide(III) and copper(II) ions leading to a tetranuclear complex. The copper(II) ion is pentacoordinate by four oxygen atoms from two bidentate *hfac-* ligands and by one nitrogen atom from the quinoline group of the radical. Preliminary results of static magnetic measurements show a typical anisotropic behavior for compounds **2** and **3** while majoritary ferromagnetic interaction was observed for **1**.

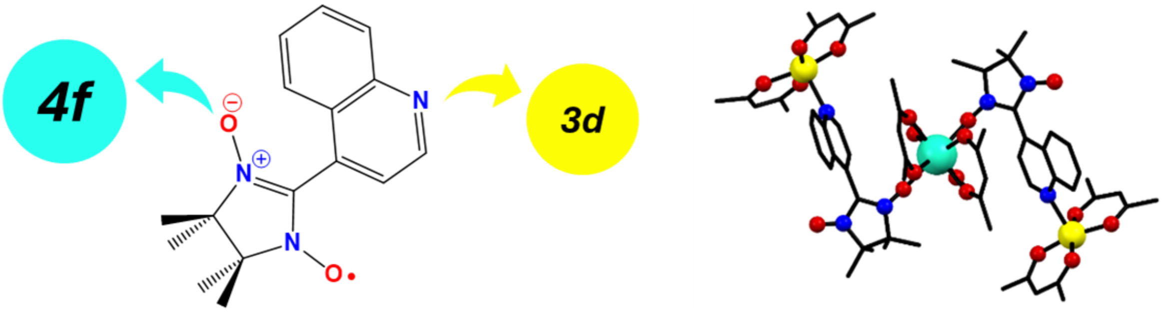

Figure 1: Hard-soft selectivity of the 4-QnNIT radical and general structure for [Ln(hfac)$_3${μ-(4-QnNIT)Cu(hfac)$_2$}$_2$]

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