

Study of Electronic Interactions in Yttrium and Gadolinium-Semiquinonato Complexes,

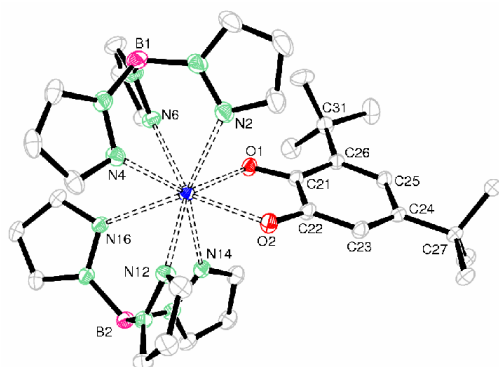
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Complexes based on ion Gd^{3+} ($S = 7/2$) and organic radicals like nitronyle-nitroxide ($S = 1/2$) present usually ferromagnetic couplings [1]. However, in the case of the $\text{Gd}(\text{HBPz}_3)_2(\text{DTBSQ})$ complex, an antiferromagnetic coupling is observed between the rare earth ion and the semiquinone radical (SQ, $S = 1/2$), corresponding to the spin state $S = 3$ [2]. This magnetic interaction was interpreted as resulting of two opposite contributions [3]: an antiferromagnetic one due to the direct overlap between the radical π magnetic orbital and the 4f orbital of the central ion, and a second one, ferromagnetic, resulting in the polarization of the 4f electrons consecutively to a partial spin transfer from the radical π orbital to the unoccupied 5d or 6s orbitals of Gd^{3+} .

In order to bring new information on the coupling mechanisms, we study the electronic interactions combining two experimental techniques: electron density modeling, based on X-rays diffraction experiment at high resolution and spin density modeling, based on polarized neutron diffraction experiment. We apply this canvas to two isomorphous complexes (Y and Gd-SQ, cf. Figure). Contrary to Gd^{3+} , as the Y^{3+} cation is spinless ($S = 0$), Y-SQ complex make possible to perceive small charge transfer between central atom and its ligands. Moreover, the topological analysis of the electron density of the yttrium complex allows to obtain precise results such as the integrated charges distribution within the material. The electron density obtained for the gadolinium complex seems to confirm the preceding results, but especially reveals difficulties in modeling the electron density related to the high atomic number of Gd atom.



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