

Evaluation of the Magnetic Interactions in Salts Containing [Ni(dmit)₂]⁻ Radical Anions

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Abstract

This paper reports on a theoretical analysis of the electronic structure and magnetic properties of the [Ni(dmit)₂]⁻ radical anions in four salt compounds resulting from the combination with supramolecular cation-crown ether assemblies. The selected compounds are representative examples of the diversity of stacking patterns and magnetic behaviors found for systems based on these [Ni(dmit)₂]⁻ anions. Difference Dedicated Configuration Interaction calculations have been performed on fragments containing two neighbor [Ni(dmit)₂]⁻ units to evaluate the intradimer, interdimer, and interchain magnetic coupling constants and analyze the electronic structure of the [Ni(dmit)₂]⁻ ions. The amplitude and sign of these through-space interactions are consistent with the structure and arrangement of the [Ni(dmit)₂]⁻ monomers in the chain and the overlap and transfer integral between the magnetic orbitals. They accurately simulate the thermal dependence of the magnetic susceptibility but do not agree with the reported J values in two of the systems, both composed by chains of weak dimers. These results highlight the nonunivocal nature of the fitting in complex systems and the difficulties in defining interaction spin models solely based on the quality of the resulting curves. This work shows the limitations of the extended Hückel calculations on the interpretation of the main ingredients of the magnetism and the relevance of reference theoretical calculations as a complementary tool for the understanding of the magnetic behavior of [Ni(dmit)₂]⁻-based functional materials.

Keywords

Chains, Crown ethers, Curve fitting, Dimers, Electronic structure, Functional materials, Ions, Magnetic couplings, Magnetic susceptibility, Nickel