

Modeling of electronic and magnetic properties of mixed-valence polyoxovanadate molecular magnets.

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Due to a large structural variety and many oxidation states of vanadium ions polyoxovanadates (POVs) exhibit rich magnetic properties and therefore find many technological applications. In sufficiently symmetric POVs some of the valence electrons are not localized at particular vanadium ions and have itinerant character. In this contribution we use the density functional theory (DFT) and effective Hamiltonian approaches to elucidate electronic and magnetic properties of a family of mixed-valence polyoxovanadate molecular magnets $X@V_{22}O_{54}$, composed of a spherical host shell $V_{22}O_{54}$ with itinerant valence electrons, and containing various diamagnetic guest anions $X=VO_2F_2^-$, ClO_4^- , SCN^- . Exploiting the synergy of the two methods and using highly efficient computational approach based on large parallel computers and an evolutionary algorithm we have managed to avoid or limit the shortcomings of the both methods (such as overparametrisation in the fitting procedure, or uncertainty of parameter estimation by DFT) and have obtained results fully concordant with each other and with the experiment. It is shown that the guest anions strongly influence the magnetism of the molecules. The number of valence electrons and their distribution varies with the type of a guest anion. Moreover, different guest anions induce different exchange interactions between shell V^{4+} ions.

References:

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