One-dimension metal molecules: Computational Methods for the investigation of delocalized interactions and magnetic coupling.

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Extended metal atom chains (EMACs), and more specifically those based upon the stabilization of linear metal backbones by polypyridylamide ligands have been recently synthesized [1]. The unique properties of these molecular wires characterized by their structural variability, their electric conductivity and their magnetic properties in the context of an emerging nanoscale technology, provide a powerful incentive toward a theoretical investigation of the family of trimetallics obtained to date with Co, Cr, Cu, Ni, Ru and Rh. The question of electron delocalization along the metal chains will be discussed. The sequence of metal orbitals obtained from DFT calculations for $M_3(dipyridylamide)_4Cl_2$ is used to delineate the general trend toward a delocalized, σ-type metal-metal bonding extending over the whole metal framework, except with M = Cu [2]. The magnetic interactions modelled by means of the broken symmetry approach are interpreted in terms of two or three magnetic orbitals, depending on the molecular oxidation state. In the case of nickel, we will discuss the superexchange mechanism coupling the terminal atoms via the central nickel, and the electronic and structural changes occurring upon a one-electron oxidation of $Ni_3(dpa)_4Cl_2$. Extrapolation to longer nickel chains is attempted [3]. For $Cu_3(dpa)_4Cl_2$, no formal metal-metal bond is present, but antiferromagnetic interactions have been characterized for the neutral as for the oxidized, mono-cationic species [4]. DFT/B3LYP calculations explain the origin of these interactions and accurately reproduce the observed J constants.

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