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# Linear trimetallic complexes with 24 d electrons: Magnetic interactions in $[Ni_3]^{6+}$ and $[Ni–Pd–Ni]^{6+}$ dipyridylamide chain complexes from density functional theory

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## Abstract

Linear chains of cobalt and nickel atoms stabilized by polypyridylamide equatorial ligands and completed at both ends with σ-donor ligands in axial position define a class of molecules in which the atomic configuration of a metal atom may depend on its position in the chain. Metal atoms occupying a central or inner position are in a square-planar environment and tend to be low spin, whereas the atoms in contact with the axial ligands at both ends of the chain experience a square-pyramidal environment and tend to be high spin. The sequence of metal orbitals arising from a trinuclear chain $M_3(dpa)_4Cl_2$ is reviewed and the population of these orbitals according to the nature of the transition metal M is sketched for $M = Cr$, Co, Ni and Cu. For $M = Ni$, the high spin state ($S = 1$) of the terminal atoms gives rise to an antiferromagnetic interaction involving four electrons, and couples these atoms via the central nickel (direct exchange) *and* via the dipyridylamide ligands (superexchange). The strength of this antiferromagnetic coupling, defined as the $-2J$ factor of the Heisenberg Hamiltonian, can be calculated within Noodleman's broken-symmetry density functional theory formalism using the B3LYP functional. Replacing the central Ni(II) atom by an isoelectronic Pd(II) does not modify the antiferromagnetic nature of the ground state, but dramatically increases the $-2J$ factor, suggesting that the properties of metal chains involving atoms of the second transition row could differ from their first row homologues. It is, however, not possible yet to decide which coupling, direct exchange, or superexchange, or both, is responsible for the surge of $-2J$.

*Keywords:* Linear chains of metal atoms; DFT; Broken symmetry; Antiferromagnetic interaction

## 1. Introduction

Chemical engineering currently produces molecular or supramolecular objects that mimic macroscopic devices at the nanometer scale. The similarity may be fortuitous, as for the well-celebrated resemblance between buckminsterfullerene $C_{60}$ and the soccer ball [1]. In most cases, however, the analogy in shape between the nano- and the macro-object has been designed and is expected to entail a similitude in the *functions* of both devices. This logical thought, which could be defined as a leap toward the limits of miniaturization, is clearly fueling the present race toward molecular machines [2]. A similar reasoning has boosted in the last 10 years the interest toward one-dimensional polymers with metal-containing backbones, considered as possible nanoscale analogues to electric wires [3,4]. Indeed, a systematic effort has been made, either to concatenate ligand-bridged dimetal precursors through unsupported metal–metal bonds [5–7] or to constrain a specific number of metal atoms to get aligned by means of purposely designed ligands [8–15]. The latter approach has been particularly successful, mainly due to the synthe-

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sis of polypyridylamides, a family of $p$-dentate ligands with general formula $[C_5H_4N{-}(N{-}C_5H_3N)_n{-}N{-}C_5H_4N]^{(n+1)-}$ and $p = 2n + 3$ [9]. On the one hand, a variety of trinuclear complexes have been characterized and extensively studied with the tridentate dipyridylamide ligand or closely related variants [10], associated with several types of axial ligands and with a large range of metals belonging to the first or second transition series (M = Co [4,10–14,16], Cr [14–16], Ni [17–20,22], Cu [21–24], Ru [24,25], Rh [24]). On the other hand, longer chains with four, five, seven and up to nine metal atoms, mainly chromium [25–27], cobalt [28,29] and nickel [13,29–33], could be assembled via the higher members of the polypyridylamide family. Quite recently, a relative estimate of the electron transfer intensity through the metal backbone of such nanowires composed of three or five atoms of $Cr^{II}$, $Co^{II}$ or $Ni^{II}$, surrounded with four appropriate polypyridylamide anions and completed with two NCS ligands in axial position, could be obtained by means of scanning tunneling microscopy (STM) [16]. The values obtained with the neutral complexes were found significantly different according to the nature of the transition metal, and these discrepancies were correlated with a tentative scheme of electron localization–delocalization among the metal centers [27,29,30]. This is to remind that "molecular wires" are more than nano-miniaturized electric conductors: they are also molecules, thus submitted to quantum effects. Moreover, they represent a very special family of transition metal complexes in which neighboring metal atoms are constrained to remain in a range of distances typically comprised between 2.25 and 2.6 Å, the variations induced by metal–metal interaction or by the lack of it being confined in this relatively narrow scope. Therefore, the structural and magnetic properties of metal chains may be governed either by the intermetallic bonding interactions or, if these interactions are not strong enough, by the electronic structure of individual metal atoms. For $d^8$ atoms such as Ni(II) or Pd(II), this electronic configuration may be either high spin or low spin, depending on their position in the chain and, as far as the outermost metal atoms are concerned, on the presence of sufficiently strong σ-donor ligands in axial position. In $Ni_3(dpa)_4Cl_2$ and for larger chains of nickel atoms stabilized by polypyridylamide ligands, this versatility results in an antiferromagnetic interaction involving four unpaired electrons localized at both ends of the chain [32] (Fig. 1).

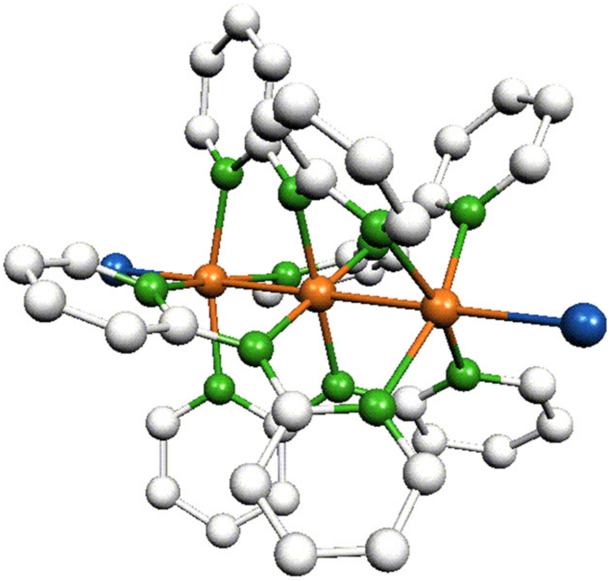

Fig. 1. Representation of a symmetric $M_3(dpa)_4Cl_2$ complex (orange: metal; blue: chlorine, green: nitrogen; white: carbon). (For interpretation of color mentioned in this figure the reader is referred to the web version of the article.)

We would like in this paper to review the status of the calculations that have presently been carried out on such linear metallic chains and dedicate a special scrutiny to a comparison between the antiferromagnetic coupling occurring in $Ni_3(dpa)_4Cl_2$ and in the isoelectronic, but still hypothetic $[Ni{-}Pd{-}Ni(dpa)_4]Cl_2$ complex.

## 2. Computational details

Calculations and geometry optimizations have been carried out with the Gaussian'98 software [34], using the formalism of the density functional theory (DFT), with the B3LYP exchange-correlation functional. Double-zeta valence basis sets have been used for all atoms, either including all electrons in the basis set for the first-row atoms (D95V bases) or describing the core of Cl and metal atoms with Los Alamos electron core potentials (LanL2DZ bases). The valence basis sets of nitrogen and metal atoms have been completed with d- and f-type polarization functions, respectively.

The antiferromagnetic singlet states of $Ni_3(dpa)_4Cl_2$ and $[Ni{-}Pd{-}Ni(dpa)_4]Cl_2$ have been characterized and their geometries optimized using the broken-symmetry (BS) formalism developed by Noodleman [35], then discussed and currently used by others [36–40]. The exchange parameter $2J_{AB}$ between two magnetic centers A and B is defined as follows by the Heisenberg–Dirac–van Vleck (HDVV) Hamiltonian [41]:

$$\hat{H}^{HDVV} = -2J_{AB}\hat{S}_A \cdot \hat{S}_B \quad (1)$$

whose eigenvalues are associated with the relative energies $E^Q = -6J_{AB}$, $E^T = -2J_{AB}$ and $E^S = 0$ for $S_A = S_B = 1$. The superscript Q, T and S refer to a quintet, a triplet and a single state, respectively.

It is clear that the nature of the ground state depends on the sign of $J_{AB}$: a positive value of $J_{AB}$, corresponding to a ferromagnetic interaction, designates the state with highest spin multiplicity as the ground state. Conversely, an antiferromagnetic interaction reverses the sign of $J_{AB}$ and the energy ordering of the spin states. In either case, the BS solution lies in between, and its energy is equal to $E_{BS} = -2J_{AB}$ if the overlap between the magnetic orbitals is neglected. It is also strongly spin-contaminated and displays in this case a value of $\langle S^2 \rangle$ close to 2.0 [37].