J. Phys. Chem. C **2007,** *111,* 618−621

Strong Antiferromagnetic Coupling at Long Distance through a Ligand to Metal Charge Transfer Mechanism

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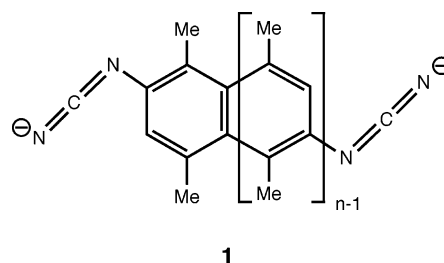Recerca i Estudis Avançats (ICREA), Barcelona, Spain*

The use of large substituted oligoacenes with dicyanoamido groups as bridging ligands should allow one to design new dinuclear transition metal complexes with relatively strong exchange interactions at very long intermetallic distances. Theoretical methods based on density functional theory predict antiferromagnetic exchange coupling constants of around 200 cm^{-1} for a nonacene Cr^{III} complex with an intermetallic distance of 33 Å, due to a ligand−metal charge-transfer mechanism. In contrast, the isoelectronic V^{II} complex in which such electron-transfer process is not allowed shows a weak ferromagnetic coupling.

Introduction

One of the main problems in molecular magnetism is the fast decay of the exchange coupling with the distance between the paramagnetic centers.[1−3] This fact introduces several limitations, for instance, for the design of new magnetic hybrid systems with large cavities and simultaneous strong exchange interactions in the host lattice. Also in most supramolecular complexes, the exchange coupling is usually rather weak because the design of the bridging ligands is basically focused on the shape of the complexes. In an attempt to design new molecular systems in which two magnetic centers communicate in a controlled way through long bridges, we have previously reported a theoretical study of a family of dinuclear transition metal complexes with derivatives of 1−3 or 1,4-dicyanamido-benzene as bridging ligands.[4] These complexes show strong exchange coupling at long distances, suitable to fine-tuning from ferro- to antiferromagnetic by design. The oxidation state of the metal has also been found to play a crucial role in determining the extent of the exchange coupling. Thus, divalent transition metal cations give an almost negligible coupling, whereas trivalent ones present considerably strong interactions. In the study presented here, we extend our previous work by analyzing the exchange coupling in polyacene-bridged complexes, extending the π system up to the nonacene derivative ($1 \leq n \leq 9$ in **1**, representing the "para" isomer). The presence of π electron donors as substituents, such as methyl groups, enhances the strength of the exchange coupling. From the experimental point of view, the largest oligoacenes synthesized and characterized by X-ray diffraction are heptacenes.[5−7]

Theoretical methods based on density functional theory using the B3LYP hybrid exchange-correlation functional[8−10] provide excellent results in the calculation of exchange coupling constants J of transition metal complexes[11−13] (through the

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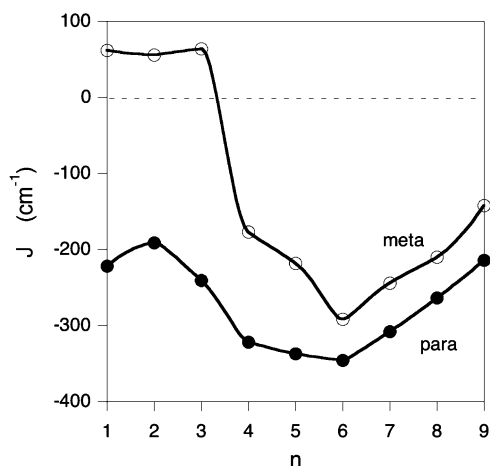
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phenomenological Heisenberg Hamiltonian $\hat{H} = -J\hat{S}_1 \cdot \hat{S}_2$) by using the Gaussian03 code[14] and all electron basis sets.[15,16] The details of the methodology employed are discussed in detail in previous publications.[17−20] Basically, we have employed a "broken-symmetry" approach[21−23] without spin projection in order to avoid the problems related with the double counting of the static correlation terms. The presence of the self-interaction error in the commonly employed functionals introduces such correlation terms.[17] The excellent results obtained so far with such an approach prompted us to apply that methodology to the prediction of the magnetic behavior of as yet unknown complexes.[4,24,25]

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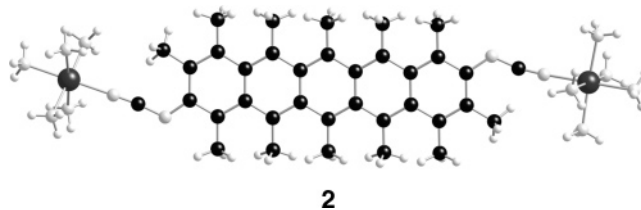
The calculated exchange coupling constants and spin populations of the metal atoms for the dinuclear Cr^{III} complexes (see, for instance **2**, the para complex $n = 5$), in which ammonia molecules were added to complete the metal coordination sphere, are represented in Figures 1 and 2 (see Table S1 in Supporting Information for the numerical values). From such results, we can draw the following conclusions: (i) The para bridging ligands provide in all cases a relatively strong antiferromagnetic coupling, whose magnitude increases with increasing length of the bridging ligand (with the exception of

Figure 1. Exchange coupling constants for $[(NH_3)_5Cr(\mu\text{-L})Cr(NH_3)_5]^{4+}$ complexes with permethylated "para" and "meta" bridging ligands as a function of the number of condensed rings in the bridging ligand (**1**).
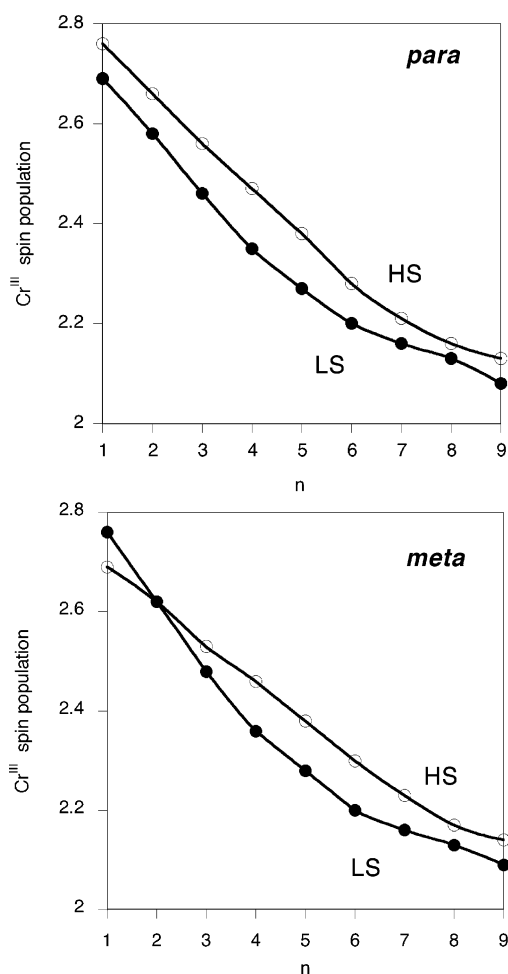

Figure 2. Representation of the Cr spin populations in the low and high spin single determinant solutions (black and white circles, respectively) for $[(NH_3)_5Cr(\mu\text{-L})Cr(NH_3)_5]^{4+}$ complexes with permethylated para (above) and meta (below) bridging ligands, as a function of the number of condensed rings in the bridging ligand (**1**).

naphthalene, $n = 2$) becomes maximum for hexacene, and decreases for longer ligands. (ii) For the meta isomers, the coupling is initially ferromagnetic and the strength of the coupling diminishes for longer bridging ligands, turning to antiferromagnetic ($J < 0$) for systems larger than anthracene. It is worth noting that, for such complexes with a large

intermetallic distance, the variation of the coupling with n is very similar to that obtained for the para isomers, showing the strongest antiferromagnetic coupling for the hexacene derivative. It is also worthy of note that antiferromagnetic coupling through nonacene is still considerably strong at an intermetallic distance of 33.1 Å. We have performed a calculation for the unsubstituted para nonacene derivative and obtained a J value of -215 cm^{-1}, almost identical to that obtained for the permethylated ligand.

To explain the results obtained we must keep in mind the presence of different processes: (i) a delocalization of the metal spin density throughout the bridging ligands due to mixing of the metal and ligand orbitals,[13,26] (ii) the spin polarization that is usually predominant in extended π systems, (iii) a ligand to metal electron-transfer that appears for large enough π systems and, (iv) the possible diradical character of long condensed aromatic systems that can be found for $n > 5$, as shown by Bendikov et al.[27] From the results represented in Figure 1, the calculated J values for the smaller systems agree well with a spin polarization mechanism as pointed out in our previous work.[4] However, an increase in the size of the π systems produces a stabilization of the low spin case resulting in a strong antiferromagnetic coupling for both meta and para isomers.

For Cr^{III}, we would expect a t_{2g}^3 electron configuration to show up as three occupied α-MO's of major d-character, with the corresponding β orbitals being empty. However, our analysis of the atomic spin densities (Figure 2) reveals that the net number of unpaired electrons per Cr atom is significantly smaller than 3, reaching a value of practically two for the longer polyacenes. The spin delocalization of the unpaired electrons of the t_{2g} orbitals over the π^* orbitals of the ligand is very small, since the α spin population for such orbitals is always close to 3. Thus, such a decrease in the net atomic spin density at the Cr atoms is due to the partial occupation of the β d_{xz} orbitals via interaction with to the π system of the bridging ligand. It is worth noting that the spin delocalization is larger or similar for the high spin states than for the low spin state in the complexes with small meta ligands that are ferromagnetic.
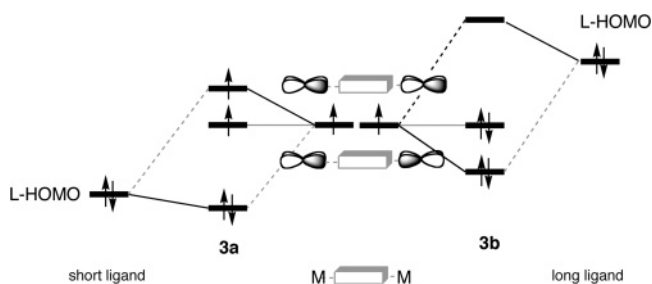
To understand the changes produced in the relevant molecular orbitals upon increasing the length of the polyacene bridge, let us focus on a simplified scheme that considers only the in-phase and out-of-phase combinations of the metal d_{xz} orbitals that are suited to interact with the π system of the meta bridging ligand (see **3**) and the π-HOMO of the bridging ligand. For a sufficiently short bridge, the π-HOMO is lower in energy than the t_{2g} orbitals, the energy ordering is qualitatively represented by **3a**, and the spin unpaired (ferromagnetic) electron configuration is expected to be competitive in energy with the antiferromagnetic, spin paired one. As we increase the size of the bridging polyacene, the energy of the π-HOMO rises, eventually surpassing the d_{xz} orbitals. Therefore, the orbital interaction is best described as in **3b** and the antiferromagnetic state is favored. That configuration implies a ligand to metal electron transfer and antiferromagnetic coupling. In fact, for
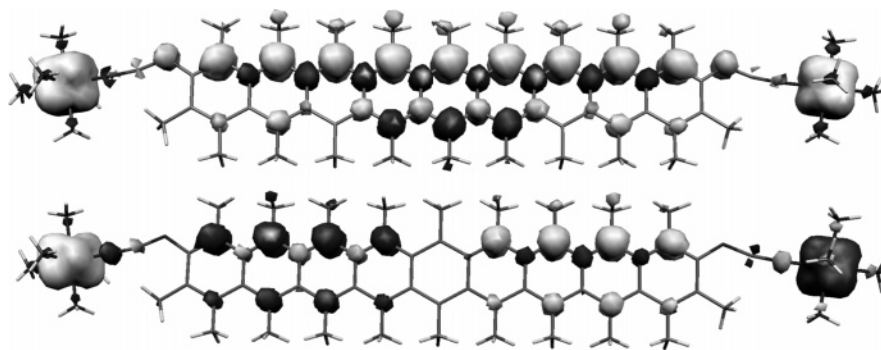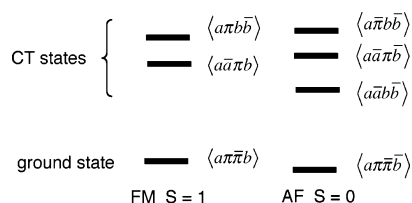
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Figure 3. Spin population plot for the high (above) and low (below) spin solutions of the meta nonacene Cr^{III} complex (clear and dark regions indicate positive and negative spin populations, respectively). The isodensity surface represented corresponds to a value of 0.002 e^-/bohr^3.

ligands of intermediate length, the π-HOMO and the d orbitals may have similar energies, and both the lowest and highest orbitals in **3b** have important contributions from both metals and bridging ligand, corresponding to a partial charge transfer, the situation depicted representing only an extreme situation.

The greater stability of the antiferromagnetic ($S = 0$) solution in comparison with the ferromagnetic ($S = 1$) state can be understood by analyzing the possible charge transfer (CT) states for a model for two orbitals *a* and *b* interacting trough a diamagnetic π system, schematically depicted in **4**. CT states corresponding to a one-electron transfer, responsible for the decreased spin population at Cr atoms with increasing *n*, appear both in the ferro- and antiferromagnetic cases and should not significantly contribute to the energy differences between them. In contrast, a two-electron CT state $\langle a\bar{a}b\bar{b}\rangle$ requires the transferred electrons to have opposite spin, according to the orbital diagram **3b**, such a situation is only allowed in the antiferromagnetic state, thus accounting for its enhanced stability relative to ferromagnetic case as we increase the size of the ligand (i.e., as we move from **3a** to **3b**). This interpretation is nicely reflected in the different size dependence of the Cr spin populations for the ferro- and antiferromagnetic states seen in Figure 2. For the very long bridges, however, the larger delocalization of the ligand's π system should result in a decreased overlap with the metal d_{xz} orbitals and progressively decaying ferro- and antiferromagnetic contributions. It is to be noted that the same charge transfer can also explain the predicted magnetic behavior of systems with functionalized nanotubes as bridging ligands, that also show strong antiferromagnetic coupling at very long distances.[28]

CT states $\left\{ \begin{array}{cc} \underline{\qquad} \langle a\pi b\bar{b}\rangle & \underline{\qquad} \langle a\bar{\pi}b\bar{b}\rangle \\ \underline{\qquad} \langle a\bar{a}\pi b\rangle & \underline{\qquad} \langle a\bar{a}\bar{\pi}b\rangle \\ & \underline{\qquad} \langle a\bar{a}b\bar{b}\rangle \end{array} \right.$

ground state $\quad \underline{\qquad} \langle a\pi\bar{\pi}b\rangle \qquad \underline{\qquad} \langle a\pi\bar{\pi}\bar{b}\rangle$

FM S = 1 $\qquad\qquad$ AF S = 0

4

In order to verify the effect of the electron-transfer mechanism on the exchange coupling constant, we have performed calculations for the isoelectronic V^{II} complexes. In this case, the d orbitals of the metal atoms are placed at higher energies due to the lower oxidation state, thus diminishing the availability of the ligand to metal charge transfer states. The calculated *J* value for the $n = 9$ complex with the meta ligand is now $+22.2$ cm^{-1}, and the spin population at the metal is 3.03 e^-, showing that upon suppression of the charge-transfer mechanism the system remains ferromagnetic with the usual spin polarization mechanism along the exchange pathway.

The analysis of the S^2 values for the low and high spin solutions (see Table S2, Supporting Information) does not show significant differences among the studied complexes, independently of the size of the π system, thus suggesting that there is not an important diradical character of the bridging ligands therein. However, we have calculated the uncoordinated para dicyanamido ligands and found an important diradical character with S^2 values ranging from 0.81 for hexacene to 1.40 for nonacene as detected by Bendikov et al. for the nonsubstituted oligoacenes.[27]

The analysis of the spin density plots in the high spin solution of the meta nonacene complex (Figure 3) shows an accumulation of α spin density along the π system of the bridging ligand due to the ligand-to-metal transfer of beta electrons. Besides, in the low spin broken-symmetry solution, that should be analyzed carefully because it is not a real state of the system, there is an alternation of the α and β spin densities along the bridge. Thus, starting from the right side, there is the metal bearing α unpaired electrons, close to this metal the bridging ligand has β spin density, and the opposite order appears in the other side of the complex. This distribution is analogous to the usual spin polarization resulting from a minimization of the electronic repulsion and maximization of the exchange integrals.[13]

Supporting Information Available: Two tables containing exchange coupling constants and spin populations represented in Figures 1 and 2, and the calculated S^2 values for the low and high spin solutions for the $[(NH_3)_5Cr(\mu\text{-}L)Cr(NH_3)_5]^{4+}$ complexes. Reference 14 in full. This material is available free of charge via the Internet at http://pubs.acs.org.

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