Exchange Coupling in Metal Complexes of the Second Transition Series: A Theoretical Exploration

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Theoretical methods based on density functional theory using hybrid functionals provide good estimates of the exchange coupling constants for complexes with metals of the second transition series, with accuracy similar to that previously obtained for complexes with lighter transition metals. The influence of the basis set and effective core potentials has been analyzed. The more diffuse nature of the 4d orbitals, in comparison with the 3d ones, considerably modifies the electronic structure and, consequently, the magnetic properties enhancing the antiferromagnetic contributions.

Introduction

In the field of molecular magnetism, the metals of the second and third transition series have been considered to be less useful than their lighter congeners due to their tendency to form low-spin complexes that in many cases are diamagnetic.[1] The heavier transition metals also tend to form complexes with strong M−M bonds that usually also present diamagnetic behavior.[2] They are also employed because of their large spin-orbit coupling that may give rise to interesting magnetic properties, although rare earth metals have been preferred in this regard.[3] For all these reasons, little is known about the magnetic properties of di- and polynuclear complexes of second and third transition series elements, even if the more diffuse character of the 4d orbitals compared to the 3d ones, the possibility of reaching higher oxidation states and the tendency to adopt larger coordination numbers should make us expect that the heavier metals have very different magnetic behavior.[2] However, during the last five years special attention has been devoted to the magnetic behavior of some complexes, mainly with molybdenum and ruthenium.[4−8]

There have been few theoretical studies of the magnetic properties of these kinds of complexes using ab initio methods. We can mention the work of Bencini et al. devoted to study of the magnetic properties of dioxobenzene-bridged Mo^{V} complexes using DFT methods.[9] Other open-shell molecules, the d^3-d^3 $[M_2Cl_9]^{3-}$ and $[M_2Cl_{10}]^{4-}$ systems ($M = Cr^{3+}$, Mo^{3+} and W^{3+}), have been exhaustively studied by Stranger et al. using DFT methods.[10−13] Semiempirical methods have been employed to analyze the exchange coupling through the Hay−Thibeault−Hoffmann model.[14] We can mention one example of complexes with second transition series elements, in this case, Koelle et al., using the extended Hückel method, analyzed the exchange coupling in $[Ru_2(\mu\text{-}Cl)_2Cp_2]$ dinuclear complexes.[15]

During the last years, we have successfully employed theoretical methods based on Density Functional Theory[16] to study the exchange coupling in several complexes containing first transition series metals.[17−20] The goal of this work is to analyze the differences in the magnetic behavior between the complexes of first and second transition series elements and to check if the accuracy in the estimation of the J values is similar to that obtained in the case of lighter transition metals.

Computational Methodology

The computational strategy adopted in previous theoretical studies on exchange-coupled dinuclear complexes has been used. For the evaluation of each coupling constant J, two separate DFT calculations are carried out, one for the highest spin state and another one for a broken-symmetry singlet state. The J values are obtained using Equation (1), where S_1 and S_2 are the total spins of the paramagnetic centers and $S_1 > S_2$ has been assumed for heterodinuclear complexes.[20]

$$E_{HS} - E_{BS} = -(2S_1S_2 + S_2)J \qquad (1)$$

The hybrid B3LYP method[21] has been used in all calculations as implemented in Gaussian-98.[22] We have previously found that, among the most common functionals,

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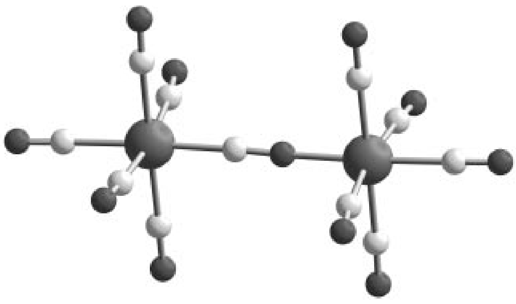
the B3LYP method combined with the broken-symmetry treatment provides the best results for calculating coupling constants.[17,20] We had also found that, when using DFT-based wavefunctions, a reasonable estimate of the low spin state energy can be obtained directly from the energy of a broken-symmetry solution. This fact is due to the inclusion of the non-dynamic correlation effects in the commonly used exchange functionals. If spin projection is applied in addition, a cancellation of such effects results, as discussed recently by Polo et al.[23]

In previous calculations of complexes with transition metal atoms we have usually employed all electron basis sets. Due to the importance of the relativistic effect of the second and third transition series elements, pseudopotentials including relativistic effects are an interesting alternative to the all-electron basis sets. We employed five different basis sets as a benchmark for a dinuclear cyano-bridged Mo^{III} complex, four of them using pseudopotentials for the Mo atoms and one with the double-ζ all-electron basis set proposed by Rappe and Goddard[24] (keyword MSV in the Jaguar code[25]). The four combinations of pseudopotentials and basis sets are as follows: (1) Stoll−Preuss quasi-relativistic pseudopotentials[26] (indicated as SDD in the Gaussian code, we also performed a test calculation with the corresponding nonrelativistic pseudopotentials for molybdenum atoms) combined with the triple-ζ all-electron basis set proposed by Ahlrichs et al.[27] for the other elements; (2) the small-core Hay−Wadt pseudopotential[28] for the Mo atom combined with the D95 all-electron basis set[29] for the first-row elements (indicated in the Gaussian code as LANL2DZ); (3) core potentials proposed by Stevens et al. for all the atoms, using a double-ζ basis set for the valence orbitals[30,31] (called CEP-31G in the Gaussian code) and, (4) the same pseudopotentials as in (3) but with a triple-ζ basis set for the valence shell[30,31] (referred to as CEP-121G in Gaussian). For the other systems with Ru and Mo atoms we have employed option (2) corresponding to the LANL2DZ basis set. Finally, for the calculations of the chromium complex we employed the same basis sets as for the cyano-bridged molybdenum complex along with a triple-ζ all-electron basis set proposed by Ahlrichs (keyword TZV in Gaussian)[27] including two p polarization functions for the chromium atom, usually done by us for first transition series metal atoms.

Results of Benchmark Systems

In order to check the accuracy of the methodology employed previously for complexes with lighter transition metals, we selected a cyano-bridged dinuclear Mo^{III} complex $[Mo_2(CN)_{11}]^{5-}$ with tetraethylammonium as a counterion, recently synthesized by Long et al.[32] (see **1**). This complex is especially interesting because the Mo^{III} cation shows a very unusual octahedral coordination, with $S_1 = S_2 = 3/2$, while Mo^{III} usually adopts structures with coordination numbers of seven or eight with the cyanide ligands.[4]



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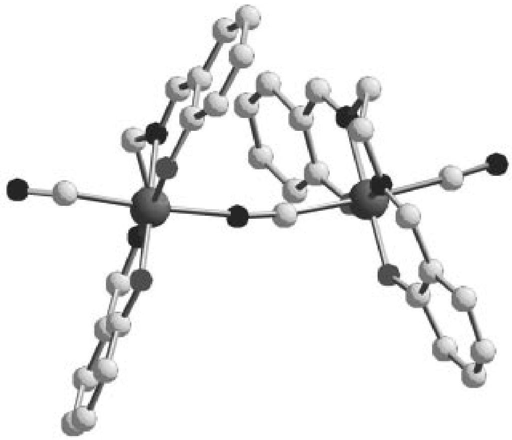
The calculated exchange coupling constants for the experimental structure of complex **1** are indicated in Table 1. All calculated values are in excellent agreement with the experimental ones. The all-electron basis set gives results similar to those obtained with effective core potentials (ecp). Thus, it seems that the relativistic corrections incorporated in the ecp are not crucial for the calculation of exchange coupling constants in these types of complexes, probably because we are calculating an energy difference and relativistic corrections of about the same magnitude affect the two spin states. This conclusion is confirmed by the value of -226 cm^{-1} obtained by using the Stoll−Preuss non-relativistic pseudopotentials for molybdenum atoms (and TZV basis set for the other atoms). This also shows the small effect of the relativistic corrections. The values of the exchange coupling constant calculated with the effective core potential are very similar, independent of the quality of the basis set employed.

Table 1. Calculated exchange coupling constants (in cm^{-1}) for complex **1** and for an equivalent symmetric Cr^{III} dinuclear complex with different basis sets and effective core potentials (ecp), together with the available experimental data[32]

	Mo^{III}	Cr^{III}
all-electron MSV	−217	−29
all-electron TZV	–	−31
ecp − SDD + TZV	−242	−27
ecp − LANL2DZ	−225	−25
ecp − CEP-31G	−247	−30
ecp − CEP-121G	−247	−29
exp.	−226	–

One of the goals of this study is to analyze the differences between the complexes of the elements of the first and second transition metal series. For this reason, we performed calculations on a symmetric cyano-bridged Cr^{III} dinuclear complex with a fixed structure (Cr−C = 2.06; Cr−N = 2.14; C−N = 1.14 Å) and the resulting *J* values can be seen in Table 1. The calculated values using pseudopotentials and an all-electron basis set are very similar as are those of the molybdenum complex, but the most remarkable result is the decrease, by an order of magnitude, of the exchange coupling constant compared to that of the Mo^{III} complex. It is also interesting to point out that the effect of using pseudopotentials is similar for Cr and Mo. Similar Cr^{III} complexes have not been reported in the literature, there is only a well-characterized cyano-bridged Cr^{III} dinuclear complex (**2**) having one salycilenealdiminato ligand per Cr^{III} cation and a terminal cyanide ligand to complete an octahedral coordination sphere.[33] We have calculated the exchange coupling constant of this complex using the all-electron basis set to check the accuracy of our calculations, and we obtain a value of -13.7 cm^{-1} to be compared with the experimental result of -11.4 cm^{-1}. The good agreement makes us confident about the J values reported for the Cr^{III} dinuclear model and confirms the weaker coupling of the Cr^{III} complexes compared to the Mo^{III} ones.



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In order to rationalize these results, we have analyzed the contributions to the exchange coupling constant by using the Hay−Thibeault−Hoffmann[14] (HTH) and Kahn−Briatt[34,35] (KB) models [Equations (2) and (3), respectively].

$$J = 2K_{ab} - \frac{(\varepsilon_1 - \varepsilon_2)^2}{J_{aa} - J_{ab}} \qquad (2)$$

$$J = 2K_{ab} + 4h_{ab}S_{ab} \qquad (3)$$

In both models, we can consider, in a rough approximation, that an antiferrromagnetic contribution (second term) depends on the square of the energy gap between the orbitals bearing the unpaired electrons (HTH model) or on the overlap between the "magnetic" orbitals (KB model). We as well as other authors[36,37] have recently shown that such magnetic orbitals are well represented by the localized orbitals of the broken-symmetry solution (we call them BS-OMSO[38]). The overall energy splitting of the six t_{2g}-type orbitals in the high-spin solution is 0.73 eV for the Mo^{III} complex and only 0.32 eV for the Cr^{III} complex. A similar result is found if we employ the KB model: the overlap between each pair of BS-OMSOs directed towards the π-system of the bridging ligand (one of them is shown in Figure 1) is 0.22 for the Mo^{III} complex and 0.05 for the Cr^{III} one. The overlap between the remaining t_{2g} orbital pair is negligible because these orbitals are perpendicular to the exchange pathway. Thus, both models predict a stronger antiferromagnetic contribution for the Mo^{III} complex, if we assume that the other terms in Equations (2) and (3) are similar. The origin of such differences can probably be found in the more diffuse character of the 4d orbitals compared with the 3d ones. To verify this assertion, we have analyzed the overlap integrals between d atomic orbitals of the metal atoms and p atomic orbitals of neighboring carbon or nitrogen atoms. We find that the overlap integrals involving the Mo atom are about one order of magnitude larger than those for Cr, both for the σ- and π-systems.

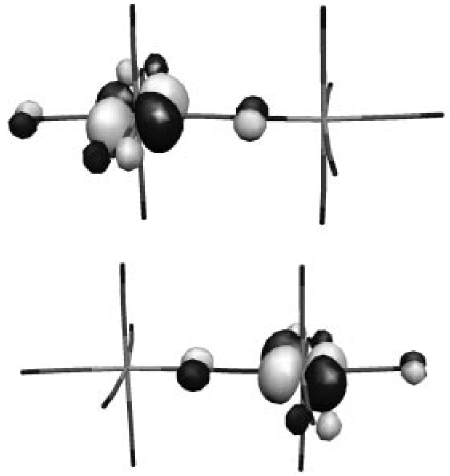
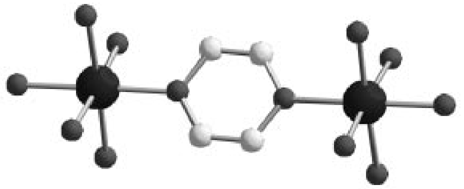


Figure 1. Broken-symmetry orbitals corresponding to one combination of the t_{2g} orbital pairs of $[Mo_2(CN)_{11}]^{5-}$ calculated at the B3LYP level

The spin population distribution also shows significant differences between the complexes of Mo^{III} and Cr^{III}. The spin population at each Mo atom is around 2.8 electrons, but 3.2 at the Cr atoms in the analogous complex. The orbital analysis shows that in both cases there is a small spin population in the formally empty e_g metal orbitals due to spin polarization of the metal−ligand bonding molecular orbitals of the same symmetry,[39] thus accounting for the spin population being larger than the number of unpaired electrons in the Cr compound. The substitution of Cr by Mo, with more diffuse atomic orbitals, results in a larger delocalization that is responsible for a smaller spin population at the molybdenum atoms.

Results of the Full Structures

We have selected two full structures to analyze the accuracy of the DFT methodology proposed for the calculation of the exchange coupling constant. The first structure corresponds to a pyrazino-bridged Ru^{III} dinuclear complex[40] (see **3**) related to the Creutz−Taube mixed-valence complex.[41] The interaction of the π-system of the pyrazine with one of the t_{2g} orbitals produces the largest stabilization due to the π-acid character of the pyrazine ligands while the one that combines slightly with the σ-system remains at an intermediate energy. Each Ru^{III} cation is low-spin d^5, and the unpaired electron is placed in the only t_{2g} orbital that interacts neither with the π-system of the bridging ligand, nor with the σ-system (see Figure 2). Therefore, the two combinations of the orbitals bearing the unpaired electron cannot have large contributions towards the bridging ligand and we expect a small energy splitting between the in-phase and out-of-phase combinations of such d orbitals and, consequently, a small exchange coupling constant for this complex. Experimentally, the authors proposed a maximum negative value for the coupling constant of -6 cm^{-1} from magnetic susceptibility measurements,[42] in very good agreement with the presently calculated value at the B3LYP level of -2.6 cm^{-1}.



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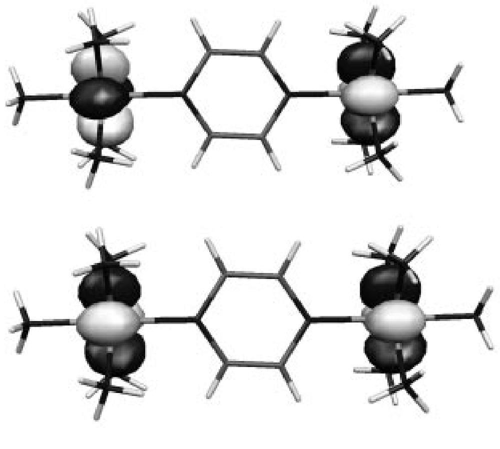
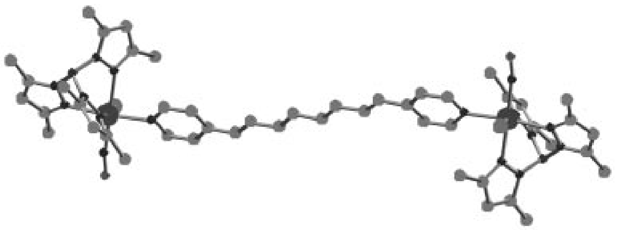


Figure 2. Orbitals bearing the unpaired electrons in the triplet state of the pyrazino-bridged Ru^{III} dinuclear complex **3** calculated at the B3LYP level

The second full structure that we have chosen is a very interesting system because it shows a strong antiferromagnetic exchange coupling between two paramagnetic centers over a long distance. It is an Mo^{V} complex with a very long dipyridylpolyene bridging ligand, complemented with nitrosyl, chloro and tris(pyrazolyl)borato ligands to complete an octahedral coordination sphere at each metal ion (see **4**).[43] The Mo−Mo distance is 20.76 Å and the exchange coupling constant between the two d^1 cations is -82 cm^{-1}, rather large considering the long distance. The authors also proposed a J value of -115 cm^{-1} using the g value obtained from EPR spectroscopy for the fitting of the magnetic susceptibility data. The problem with the experimental data is that it was only measured between 80 and 300 K. We have calculated a somewhat smaller value of -31 cm^{-1}, which nevertheless shows the ability of the present calculations to correctly describe the nature (antiferromagnetic) and approximate magnitude of exchange interactions at very long distances between two Mo^{V} centers.



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Along the same lines, we have recently predicted with the same methodology that some transition metal complexes with long dicyanamidobenzene-type bridging ligands can show very strong ferromagnetic or antiferromagnetic coupling depending on the isomer and substituents of the bridging ligand.[44] In the same study we have analyzed, from an orbital point of view, the exchange coupling for systems with long conjugated bridging ligands that have usually only been analyzed in terms of the so-called spin polarization mechanism using a McConell model.[45] Our conclusions indicated that usually for a symmetric bridging ligand with an even number of atoms in the exchange pathway, such as that in complex **4**, the two ligand orbitals that combine with the two metal orbitals have different energies. Thus, the two molecular orbitals corresponding to the whole molecule show a sizeable energy splitting, resulting in a large antiferromagnetic contribution, according to the HTH model (see Figure 3). If the bridging ligand has an odd number of atoms, the orbitals remain nearly degenerate and the coupling would be ferromagnetic. For the dipyridylpolyene ligand, the calculated orbital energies are non-degenerate (energy splitting of 0.07 eV equivalent to 550 cm^{-1}) due to different π-bonding or antibonding character at the central C−C bond of the two orbitals, confirming those rules.

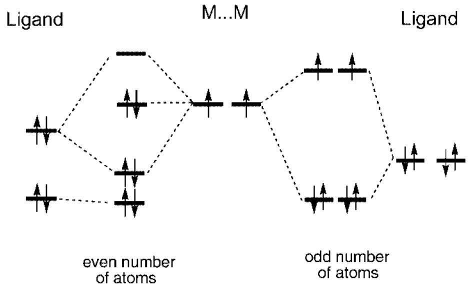

Figure 3. Scheme of the orbital interaction of a dinuclear transition metal complex through a bridging ligand depending on the number of atoms of the bridging ligand

Conclusions

The exchange coupling constants for different complexes of second series transition elements have been calculated using a theoretical method based on density functional theory. The use of the hybrid B3LYP functional, as in previous studies devoted to complexes with metals of the first transition series, offers very good results. The influence of the basis set and different effective core potentials on the calculated J value is very small and results obtained with all-electron basis sets or with pseudopotentials are quite similar. The comparative analysis of the electronic structures of the $[Mo_2(CN)_{11}]^{5-}$ and $[Cr_2(CN)_{11}]^{5-}$ complexes reveals the importance of the more diffuse nature of the 4d orbitals of the molybdenum atoms. This fact results in a larger antiferromagnetic contribution that can be understood using the Hay−Thibeault−Hoffmann or Kahn−Briatt models, i.e., a larger energy splitting of the orbitals bearing unpaired electrons or a larger overlap between the localized "magnetic" orbitals, respectively. The study of the spin population distribution also shows a considerably larger delocalization in the case of the Mo^{III} complex due to the more diffuse character of the 4d orbitals.

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