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Theoretical Study of the Relationship between the Nearest-Neighbor Exchange Coupling Interactions and the Number of Peripheral Complexes in the Cyano-Bridged $CrMn_6(CN)_6$ and $CrMn_2(CN)_2$ Clusters

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A theoretical density functional study of the relationship between the nearest-neighbor constants and the number of peripheral complexes in the cyano-bridged $[Cr[CNMn(salen)(H_2O)]_6]^{3+}$ and $[(5\text{-}Brsalen)_2(H_2O)_2Mn_2Cr(CN)_6]$ clusters is presented. Two approaches show that the antiferromagnetic coupling interactions between nearest neighbors decrease with the increase of the number of peripheral complexes, although the second approach provides better results using several exchange-correlation functionals. The first approach consisted of evaluating the exchange coupling constant J_{ij} between two paramagnetic metal centers *i* and *j* in the hexanuclear molecule by calculating the energy differences between the highest and broken-symmetry spin states of a model molecule in which metal atoms except for *i* and *j* are substituted by diamagnetic Zn(II) cations, while the second consisted of calculating the different spin-state energies of hexanuclear complexes and using the Heisenberg Hamiltonian to obtain the exchange coupling constants between different metal centers. Moreover, Kahn's qualitative theory succeeded in being applied to interpret the trend.

Introduction

In recent years, the synthesis and study of single-molecule magnets with high total spin that can be used to store potential data has received much attention.[1−10] Among these single-molecule magnets, cyanide single-molecule magnets are the most extensively studied families experimentally because of their special structures. Many cyanide single-molecule magnets with different first and second transition-metal centers have been synthesized.[5−9] However, a lot of theoretical studies on single-molecule magnets were often limited to homopolynuclear clusters such as Mn_4,[10] Mn_{10},[11] V_{15},[12] Ni_6[2], and Cu_6[2] clusters. Few theoretical studies on cyanide heteropolynuclear clusters have been found, to our knowledge. To extend the research of the cyanide heteropolynuclear single-molecule magnets, we will investigate the magnetism of the cyano-bridged single-molecule magnet $[Cr[CNMn(salen)(H_2O)]_6]^{3+}$ [6] using density functional theory (DFT).

Long and co-workers found that the absolute nearest-neighbor constants *J* diminish as the number of peripheral complexes connected to the central ions increase for a series of cyano-bridged Mn(II)−Cr(III),[8,13] Mn(III)−Cr(III),[5,6] Mn(II)−Mo(III),[7] Mo(III)−Ni(II),[9] and Cr(III)−Ni(II)[14,15] complexes. To inspect whether the absolute nearest-neighbor constants *J* always diminish as the number of peripheral complexes increases for the above complexes, we selected the cyano-bridged $[Cr[CNMn(salen)(H_2O)]_6]^{3+}$ cluster[6] (complex **I**) and the linear trinuclear $[(5\text{-}Brsalen)_2(H_2O)_2Mn_2Cr(CN)_6]$ cluster[5] (complex **II**) to investigate the relationship between the exchange coupling constants *J* and the number of peripheral complexes. Also, Kahn's qualitative theory[16] was used by us to interpret the relationship. Finally, we will discuss the relationship between the calculated spin density populations on Cr(III) or Mn(III) and the number of peripheral complexes.

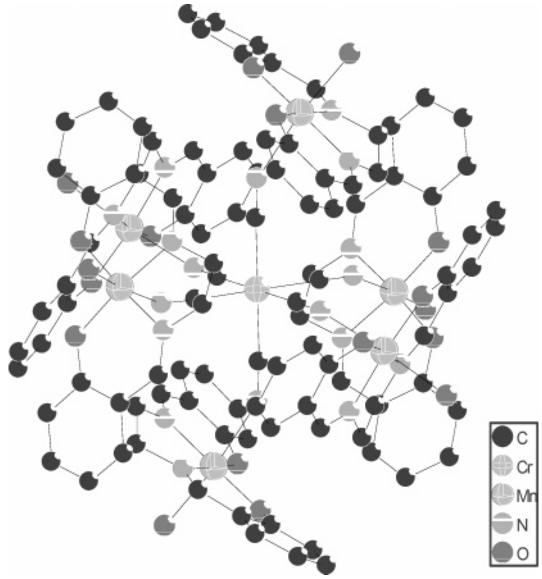

Figure 1. Structure of complex **I**.

Computational Methodology

Description of the Complexes and Models. Complex **I**[6] $\{Cr[CNMn(salen)(H_2O)]_6\}^{3+}$ is a polynuclear cluster in which a central $[Cr(CN)_6]^{3-}$ unit is coordinated through each of its nitrogen atoms to a salen-bound Mn(III) center (see Figure 1; H atoms are omitted.).

Complex **II**[5] $[(5\text{-}Brsalen)_2(H_2O)_2Mn_2Cr(CN)_6]^-$ is a trinuclear cluster wherein an octahedral $[Cr(CN)_6]^{3-}$ complex is sandwiched between a pair of $[Mn(5\text{-}Brsalen)(H_2O)]^+$ units (see Figure 2; H and Br atoms are omitted).

Models **A** and **B** (see Figure 3) are the modeled structures which only include one peripheral complex of complexes **I** and **II**, respectively.

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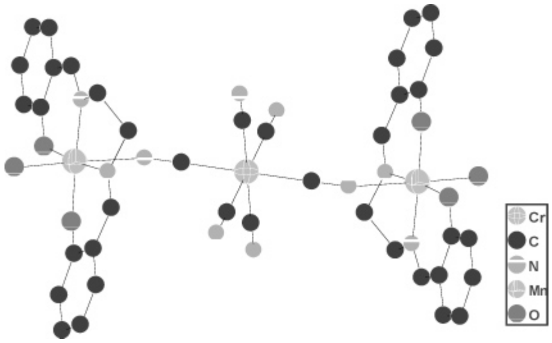


Figure 2. Structure of complex **II**.

Models $\mathbf{A^1}$, which was obtained by substituting the phenyl rings of model **A** with a localized HC═CH, $\mathbf{A^2}$ (including two peripheral complexes), $\mathbf{A^3}$ (including three peripheral complexes), $\mathbf{A^4}$ (including four peripheral complexes), $\mathbf{A^5}$ (including five peripheral complexes), and $\mathbf{A^6}$ (including six peripheral complexes) (see Figure 4) were used to investigate the relationship between J_{12} and the number of peripheral complexes.

All the models were directly taken from complexes **I** and **II** and not optimized, because small changes to the experimental structures could result in significant deviations for the coupling constants.

Calculation of Exchange Coupling Constant. Now, there are two different approaches to calculate the exchange coupling constants for the polynuclear complexes.[2−4] In all calculations, the spin−orbit coupling is not considered, so the magnetic anisotropy need not be considered. The first approach consisted of evaluating the exchange coupling constant J_{ij} between two paramagnetic metal centers i and j in the hexanuclear molecule by calculating the energy difference between the highest and broken-symmetry spin state of a model molecule in which metal atoms except for the above i and j are substituted by diamagnetic Zn(II) cations. This approach was used to calculate the exchange coupling interactions of hexanuclear complexes in many papers and has proven to give good results compared to the experimental ones.[2−4,17] The second approach is to calculate the different spin-state energies of hexanuclear complexes and use the Heisenberg Hamiltonian to obtain the exchange coupling constants between different metal centers.[2−4,17,18] It is the more rigorous approach in evaluating J for polynuclear complexes with respect to the first one. These two approaches will be interpreted thoroughly below.

At first, we interpret the first approach. The magnetic interactions between Mn(III)and Cr(III) metal ions were studied on the basis of density functional theory (DFT) coupling with the broken-symmetry approach (BS).[19] The exchange coupling constants J have been evaluated by calculating the energy difference between the high-spin state (E_{HS}) and the broken-symmetry state (E_{BS}). Assume the spin Hamiltonian is defined as

$$\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2 \tag{1}$$

According to the recent experience of Ruiz et al. based on a number of calculations on the magnetic exchange coupling constants with the broken-symmetry approach,[20−22] E_{BS} may be regarded as an approximation of the energy of the lowest spin state. Considering that local functionals overestimate the relative stabilization of the lowest spin state relative to the highest spin state,[23] DFT will usually give larger J values than experimental ones.[24] So, Ruiz et al.[21] put forward eq 2 to calculate J.

$$2J = \frac{E_{\mathrm{BS}} - E_{\mathrm{HS}}}{2S_1S_2 + S_2} \tag{2}$$

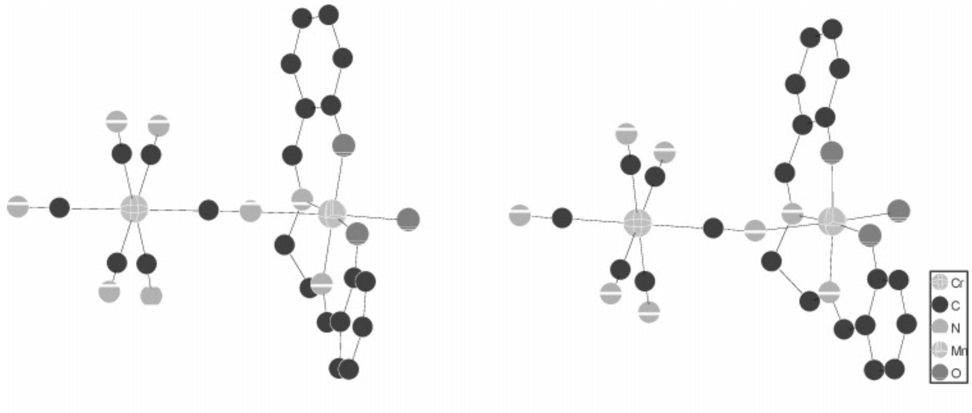
However, this formula corresponds strictly to the limit of complete overlap between the magnetic orbitals, and such a hypothesis is not sustained,[25] although it can give good J results compared to experiment.[20−22]

In a recent work, Dai et al.[26] examined the eigenstates of the Heisenberg spin Hamiltonian $\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$ and the Ising spin Hamiltonian $\hat{H}^{\mathrm{Ising}} = -2J\hat{S}_{1z}\hat{S}_{2z}$ for a general spin dimer consisting of M unpaired spins at one spin site and N unpaired spins at the other spin site. Their work showed that the description of the highest-spin and broken-symmetry spin states of a spin dimmer by $\hat{H}$ is the same as that by $\hat{H}^{\mathrm{Ising}}$. For the analysis of spin exchange interaction of a magnetic solid on the basis of density functional theory, the use of the Heisenberg spin Hamiltonian in the "cluster" approach is consistent with that of the Ising spin Hamiltonian in the "noncluster" approach. They put forward eq 3 according to the Heisenberg spin Hamiltonian to calculate J. However, the same expression is also obtained by considering the energies of the HS and BS spin states on the basis of the Ising spin Hamiltonian. For

$$J = \frac{E_{\mathrm{BS}} - E_{\mathrm{HS}}}{MN} \tag{3}$$

complexes **I** and **II**, where $M = 4$ for Mn(III) and $N = 3$ for Cr(III), from eq 3 we further get the expression

$$J = (E_{\mathrm{BS}} - E_{\mathrm{HS}})/12 \tag{4}$$



A **B**

Figure 3. Structures of models **A** (left) and **B** (right).

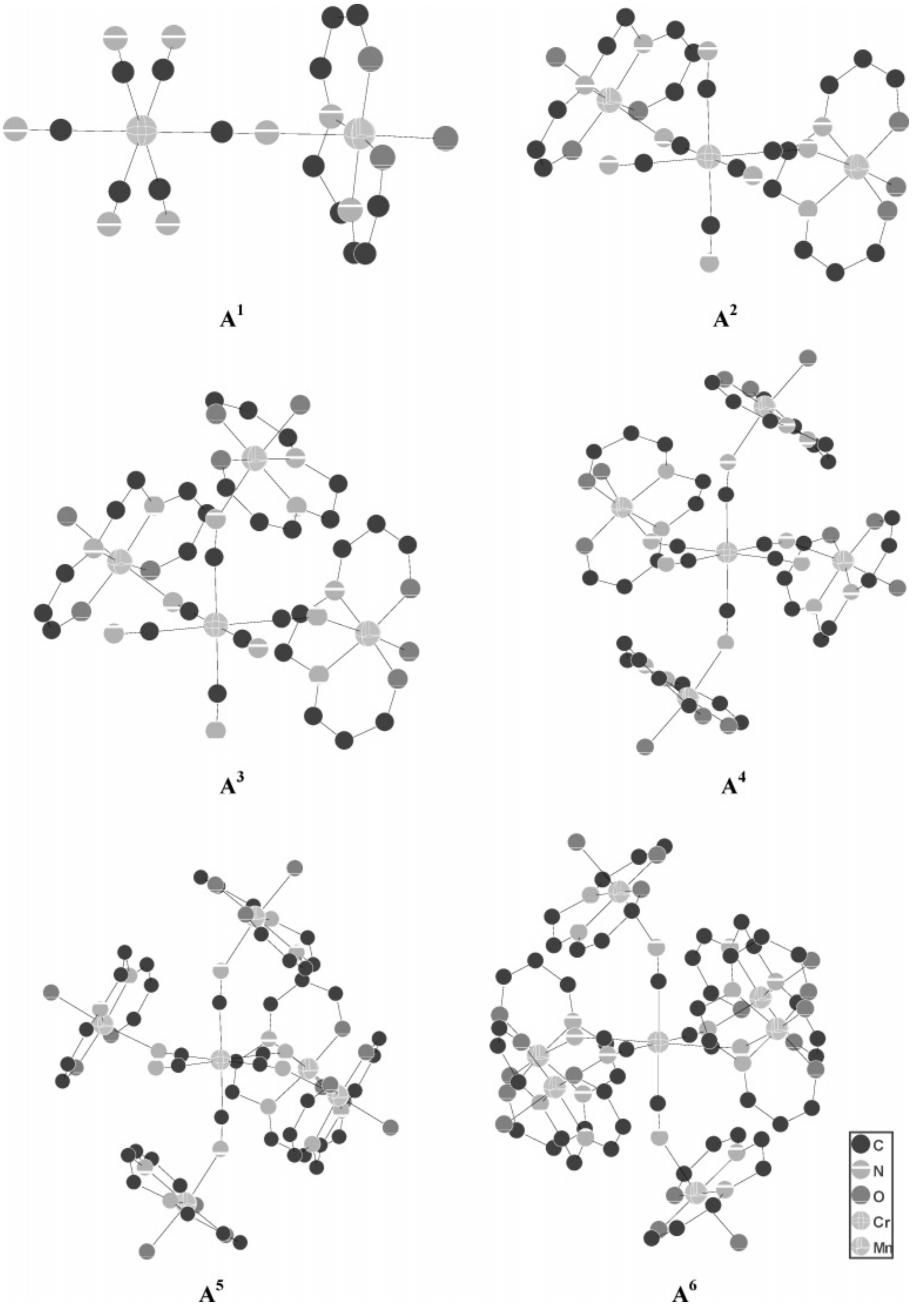

A^1 **A^2** **A^3** **A^4** **A^5** **A^6**

Figure 4. Structures of models **A^1**, **A^2**, **A^3**, **A^4**, **A^5**, and **A^6**.

Equations 3 and 4 are only used for binuclear compounds. In the calculations of the polynuclear complexes using the first approach, we used a diamagnetic Zn(II) to replace one of the Mn(III); the resulting $CrMnZn_{1-5}$ complex is equivalent to a binuclear CrMn complex from the magnetic point of view, and so, we can use eqs 3 and 4 to obtain the exchange coupling constants J_{12}.

Then, we interpret the more rigorous second approach. If one neglects spin−orbit coupling effects, the Hamiltonian for a general extended structure is indicated as

$$\hat{H} = \sum_{i>j} - 2J_{ij}\hat{S}_i\hat{S}_j \tag{5}$$

where $\hat{S}_i$ and $\hat{S}_j$ are the spin operators of the different paramagnetic centers. The J_{ij} values are the coupling constants between all the paramagnetic centers. In our paper, we only consider the exchange interactions between nearest neighbors. This fact together with the presence of additional symmetry elements in the structure results normally in a reduced set of J_{ij} values. When using single-determinant methods such as DFT, the calculated energies are related to the diagonal matrix elements of the Heisenberg Hamiltonian. An alternative way to describe the system is by considering an Ising Hamiltonian as a special case of an Heisenberg Hamiltonian in which only the diagonal terms are kept. Thus, we can consider that the wave functions obtained with the single-determinant methods are eigenfunctions of an Ising Hamiltonian that is formulated with the same J values as the original Heisenberg Hamiltonian,

Figure 5. Two spin states: **1** with $S = {}^5/_2$ (left), **2** with $S = {}^{11}/_2$ (right) for complex **II**.

because their diagonal terms are identical. For that reason, the J values obtained with single-determinant methods are directly comparable to those obtained from experimental data.[4] So, we can use the single-dominant method DFT to obtain the J values from calculating the energy differences between two spin states. A thorough description of this approach can be found in refs 2−4 and 18.

For complex **II**, which includes three magnetic centers, the magnetic coupling constants J_{12} between each nearest-neighbor Cr(III)−Mn(III) pair are the same for the symmetry in the structure of complex **II**. Moreover, we only need the nearest-neighbor coupling constant. So, the J_{12} can be extracted by calculating the energies of two spin states: **1** with $S = {}^5/_2$ and **2** with $S = {}^{11}/_2$, which are shown in Figure 5. The equation to extract the J_{12} is thus

$$J_{12} = (E_1 - E_2)/27 \qquad (6)$$

To obtain all the nearest-neighbor constants J_{12} for the modeled structures $\mathbf{A}^2$, $\mathbf{A}^3$, $\mathbf{A}$,^{4} $\mathbf{A}^5$, and $\mathbf{A}$,^{6} we also only need to calculate the energies of two spin states for each model. Two spin states for each model are as follows: **1** with $S = {}^5/_2$ and **2** with $S = {}^{11}/_2$ for $\mathbf{A}^2$; **1** with $S = {}^9/_2$ and **2** with $S = {}^{15}/_2$ for $\mathbf{A}^3$; **1** with $S = {}^{13}/_2$ and **2** with $S = {}^{19}/_2$ for $\mathbf{A}^4$; **1** with $S = {}^{17}/_2$ and **2** with $S = {}^{23}/_2$ for $\mathbf{A}^5$; and **1** with $S = {}^{21}/_2$ and **2** with $S = {}^{27}/_2$ for $\mathbf{A}^6$. For all the above states for **1**, only the spins on Cr(III) are flipped. The equations to extract J_{12} values for all the models are as follows:

$$\text{For model } \mathbf{A}^2\text{, the equation is thus} \quad J_{12} = (E_1 - E_2)/27 \qquad (7)$$

$$\text{For model } \mathbf{A}^3\text{, the equation is thus} \quad J_{12} = (E_1 - E_2)/39 \qquad (8)$$

$$\text{For model } \mathbf{A}^4\text{, the equation is thus} \quad J_{12} = (E_1 - E_2)/51 \qquad (9)$$

$$\text{For model } \mathbf{A}^5\text{, the equation is thus} \quad J_{12} = (E_1 - E_2)/63 \qquad (10)$$

$$\text{For model } \mathbf{A}^6\text{, the equation is thus} \quad J_{12} = (E_1 - E_2)/75 \qquad (11)$$

DFT calculations have been performed using the Amsterdam Density Functional (ADF, version 2004.01[27]) package for four models. Illas et al.[28] showed the strong dependence of the calculated J with respect to the exchange-correlation functional chosen. Several exchange-correlation functionals will be used to evaluate J. In the calculations of J using ADF, the local density approximation (LDA) made use of the Vosko, Wilk, and Nusair[29] (VWN) local-correlation functional. A series of generalized gradient approximations (GGA), Perdew−Wang 1991 (PW91),[30] Perdew−Burke−Ernzerhof (PBE),[31] and recently developed OPTX−Perdew (Operdew),[32] and OPTX−Perdew−Burke−Ernzerhof (OPBE)[31,32] functionals, were examined. Basis set TZV2P (a basis set of triple-ξ quality[33] supplemented with two p orbitals ("polarization functions")) was applied for all of the metals (Mn, Cr) and basis set DZP (a basis set of double-ξ quality[33] supplemented with one polarization function) for the other atoms (C, N, and H). The inner core shells of C(1s), N(1s), Zn(1s, 2s, 2p), Mn(1s, 2s, 2p), and Cr(1s, 2s, 2p) were treated by the frozen core approximation. In calculations, we did not use meta-GGA and hybrid GGA functionals, because they may give wrong results if used in combined with frozen core approximation (meta-GGA and hybrid GGA functionals need a kinetic energy term that is related to all orbitals) in ADF2004.01.[27] The accuracy parameter (accint) for the numerical integration grid was set to 4.0 for all of the complexes. The convergence standard of the system energy was set to be smaller than 10^{-6} eV, reaching a precision required for the evaluation of J.

TABLE 1: Calculated J_{12} Values (cm^{-1}) for A, A^1, B, and II and Experimental J_{12} Values (cm^{-1}) for Complexes I and II Using Different Functionals in ADF

	first approach (BS-DFT)				second approach
	A	**A^1**	**B**	**II**	**II**
VWN	−248.2	−251.4	−239.7	−136.5	−49.2
PW91	−209.4	−207.1	−200.9	−107.2	−30.6
PBE	−207.6	−204.9	−198.9	−106.9	−30.8
Operdew	−117.3	−96.0	−124.3	−61.9	−8.6
OPBE	−121.2	−99.5	−127.2	−66.6	−10.8
exptl	−2.5[6]		−6.3[5]		

Results and Discussion

Relationship Between J_{12} and the Number of Peripheral Complexes. The calculated and experimental J values are shown in Table 1.

For models **A** and **B**, which only include one peripheral complex of complexes **I** and **II**, respectively, the calculated results using different functionals with the first approach have small differences. However, from the experimental data, the intramolecular antiferromagnetic interactions of complex **I** are weaker than those of complex **II**.[5,6] So, the accurate calculations of the J_{12} for complexes **I** and **II** will be carried out. Also, the relationship between the nearest-neighbor CrMn constant J_{12} and the number of peripheral complexes was investigated.

To evaluate the above two approaches on calculating the J values of polynuclear complexes, we first calculated the nearest-neighbor coupling constant J_{12} values of the complete structure **II**. The calculated absolute J_{12} values using the first approach with several LDA and GGA functionals all decrease with the increase of the number of peripheral complexes with respect to that of model **B** (see Table 1). Moreover, to obtain the more accurate J_{12} values for complex **II** using the second approach, we calculated the energy of two spin states, **1** with $S = {}^5/_2$ and **2** with $S = {}^{11}/_2$, which are shown in Figure 5 and used eq 6 to calculate the J_{12} (see Table 1). The calculated results using several XCs are all better than those using the first approach. This is because using Zn(II) to replace Mn(III) in the first approach will ignore the influence of the other Mn(III) on the interactions between the nearest-neighbor CrMn. Such results were also found in refs 2−4. It can be seen that there is a good agreement between the calculations using recently developed Operdew[31] and OPBE[30,31] functionals and experimental J_{12} values. However, the two approaches both show that the nearest-neighbor exchange interactions weaken with the increase of the peripheral complex.

For simplification, we use model $\mathbf{A}^1$ (Figure 4) which was obtained by substituting the phenyl rings of models **A** (Figure 3) with the localized HC═CH. From the calculated J values of model $\mathbf{A}^1$ with several XCs, they have little difference from those of **A** (see Table 1). So, models $\mathbf{A}^2$, $\mathbf{A}^3$, $\mathbf{A}^4$, $\mathbf{A}^5$, and $\mathbf{A}^6$ (Figure 4) containing two, three, four, five, and six peripheral complexes of complex **I**, respectively, were used to investigate

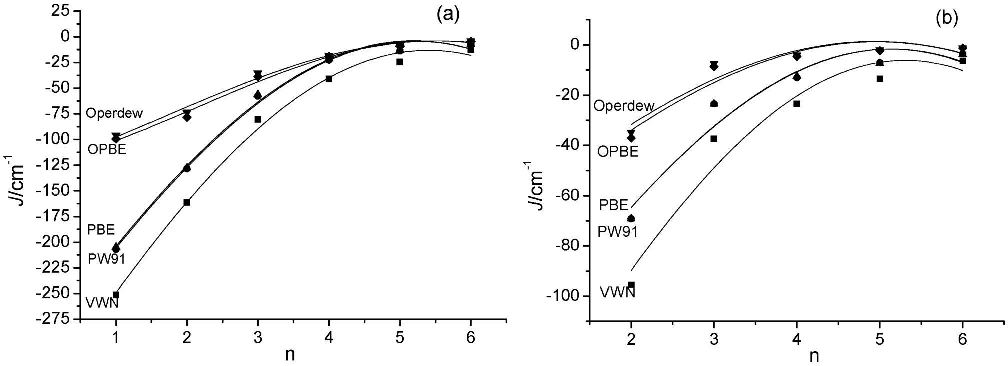


Figure 6. Relationship between the nearest-neighbor interaction constant J_{12} (cm^{-1}) and the number of peripheral complexes *n* with several functionals (VWN (■), PW91 (●), PBE (▲), Operdew (▼) and OPBE (◆)) for the models of complex **I**. (a) the relationship using the first approach; (b) the relationship using the second approach.

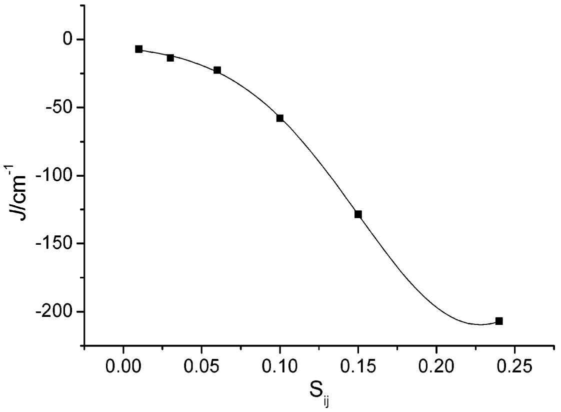


Figure 7. Relationship between the nearest-neighbor interaction constant J_{12} (cm^{-1}) and the mean overlap integral S_{ij} with the increase of the number of peripheral complexes using PW91 functional for the models of complex **I**.

the relationship between J_{12} and the number of peripheral complexes. Two approaches with several LDA and GGA functionals were used to investigate the relationship which is shown in Figure 6 where the absolute J_{12} values all decrease with the increase of the number of peripheral complexes.

The second approach also gives better results than the first one. From the calculated J_{12} values, the consistent behavior between the calculated *J* and the experimental value improves in the sequence of the LDA (VWN), the GGA (PW91 and PBE), and the GGA (OPerdew and OPBE), in general, which was also found in ref 35. For model $\mathbf{A^6}$, which is the most similar to the complete structure **I**, the calculated J_{12} values using the second approach with Operdew and OPBE functionals are also the nearest to the experimental result.

Qualitative Analysis of the Exchange Interaction. According to Kahn's theory,[16] the exchange coupling constant *J* is expressed in eq 12 ($\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$). The positive term, K_{ab},

$$J_{ab} \approx K_{ab} - S_{ab}(\Delta^2 - \delta^2)^{1/2} \qquad (12)$$

represents the ferromagnetic contribution J_F, favoring parallel alignment of the spins and a triplet ground state, while the negative term $-S_{ab}(\Delta^2 - \delta^2)^{1/2}$ is the antiferromagnetic contribution J_{AF}, favoring antiparallel alignment of the spins and a singlet ground state. S_{ab} is the overlap integrals between **a** and **b**. δ is the initial energy gap between the magnetic orbitals, Δ the energy gap between the molecular orbitals derived from them. When several electrons are present on each center, n_A on one side and n_B on the other, *J* can be described by the sum of the different "orbital interactions" as J_{ab}, defined as above for pairs of orbitals **a** and **b** located on each site, weighted by the number of electrons

$$J = \Sigma_{a,b} J_{ab}/n_A \times n_B \qquad (13)$$

Some authors[36,37] have recently shown that magnetic orbitals **a** and **b** are well-represented by the localized orbitals of the broken-symmetry solution (they call them BS-OMSO[38]). There are twelve different contributions to the exchange coupling constant in each Cr(III)−Mn(III) pair; the inappropriate orientation of some the magnetic orbitals involved allows us to discard most of them. The ferromagnetic contributions are not considered, because the antiferromagnetic coupling interactions for all the complexes are dominant. Moreover, as usual, the changes in the J_{AF} term are more important, and these contributions will usually control the magnetostructural correlations, especially for those whose intramolecular interactions are antiferromagnetic. Also, we found that, although the ferromagnetic term J_F may contribute 20% or 30% to the exchange coupling interaction, the variation of J_F with the increase of the number of peripheral

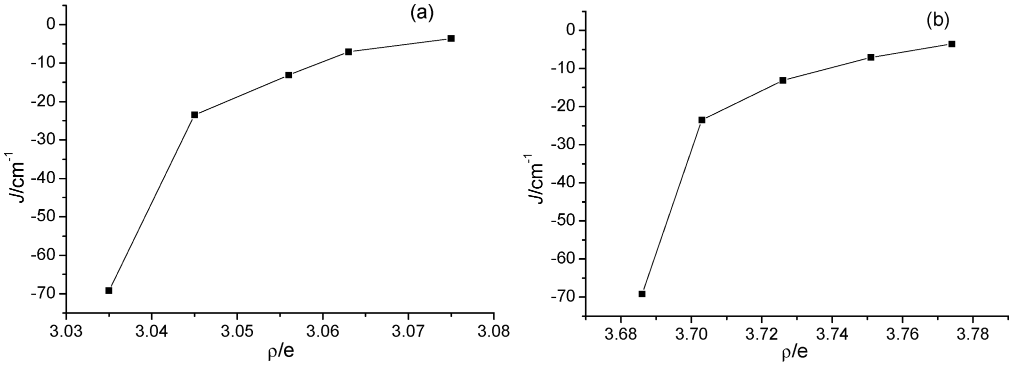


Figure 8. Relationship between the nearest-neighbor interaction constant J_{12} (cm^{-1}) and the spin density populations ρ on Cr(III) (Figure 8a) and Mn(III) (Figure 8b) in the high-spin states with PW91 functional for the models of complex **I** using the second approach.

complexes is small compared to that of J_{AF} and can be neglected. Hence, we only considered the changes in the J_{AF} term. Among the important antiferromagnetic contributions, the most relevant ones are those involving two t_{2g} orbitals (d_{xy} and d_{xz}) of the Cr(III), which are directed toward the bridging ligand because of the good overlap with the appropriate t_{2g} orbitals (d_{xy} and d_{xz}) of the Mn(III). The mean overlap integral S_{ij} between the four orbitals of the Cr(III) and Mn(III) can be expressed as

$$S_{ij} = {}^{1}/_{4}(d_{xy}d_{xy} + d_{xy}d_{xz} + d_{xz}d_{xy} + d_{xz}d_{xz}) \qquad (14)$$

Figure 7 gives the relationship between J_{12} and S_{ij} obtained using eq 14 and the PW91 functional with the increase of the number of peripheral complexes.

The absolute J_{12} values decrease with the decrease of S_{ij} in accordance with Kahn's qualitative theory. Therefore, we can conclude that the increase of the number of peripheral complexes will decrease the overlap integral S_{ij}. The above conclusion can also be verified by investigating the relationship between J_{12} and the spin density populations on Cr(III) and Mn(III) with the increase of the number of peripheral complexes. Because the spin density populations on several Mn(III) are almost the same, we only use the spin density population on one of Mn(III). The relationship is shown in Figure 8a,b where the spin density populations on Cr(III) and Mn(III) obtained with Mulliken Population Analysis[39] calculated using the PW91 functional in the ADF2004.01 package in the high-spin (HS) state increase with the increase of the number of peripheral complexes, and consequently, the S_{ij} decreases and then the absolute J_{12} decreases in accordance with Kahn's theory.

The above results were calculated using the second approach. The first approach also gives the same trend.

Conclusions

Two approaches were used to investigate the magnetic coupling interactions between the nearest-neighbor Cr(III) and Mn(III) for complexes **I** and **II**. From our calculations, although the second approach gives better J_{12} values than those using the first approach, the two approaches both show that the antiferromagnetic interactions between nearest neighbors decrease with the increase of the number of peripheral complexes for our studied Cr(III)−Mn(III) systems. The trend is rationalized by using Kahn's theory through the overlap integral S_{ij} and the spin density populations on Cr(III) and Mn(III) in the HS states successfully. Our calculations will be of help in understanding the same trend found in a series of other cyano-bridged transition-metal complexes in which the intramolecular interactions are antiferromagnetic, although such a trend is system-dependent.

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