

## Mixed-valence trinuclear manganese clusters: Influence of the electronic transfer on the magnetic properties

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The magnetic behavior of mixed-valence trinuclear clusters  $d^4-d^4-d^5$  is discussed on the basis of a model which takes into account valence delocalization and Heisenberg exchange. This model considers the competing effect between the electronic transfer and the localization of the extra electron due to an asymmetry of the triangular entity. The magnetic properties of the mixed-valence oxo-centered Mn(II)-Mn(III)-Mn(III) complexes formulated as  $Mn_3O(O_2CR)_6L_3$  ( $R = Me$ ,  $L =$  pyridine) are discussed on the basis of the developed model, supporting a significant intramolecular electron transfer. A comparison of these results to those previously reported by assuming a valence-trapped model is given.

### I. INTRODUCTION

The problem of determining the energy spectrum and magnetic behavior of exchange-coupled polymetallic systems has now become quite trivial when the electrons remain localized on each metallic center. The situation appears to be more complex in exchange-coupled mixed-valence systems, due to the possibility of the electrons to undergo a rapid hopping between the metallic centers. Such electronic transfers have been accounted in two and three center mixed-valence systems using the double exchange theory.<sup>1,2</sup> This assumes an "extra" electron equally delocalized between identical magnetic sites (containing the valence electrons).

We have recently proposed a more versatile approach involving all particles, without distinction between valence and itinerant electron.<sup>3,4</sup> In such cases, in addition to the magnetic exchange, the electronic transfers have to be taken into account. In this work, this model is generalized to mixed valence trinuclear manganese clusters.<sup>5-7</sup>

### MODEL

According to the geometry of the  $Mn_3O$  complexes,<sup>5-7</sup> we consider a three center triangular  $d^4-d^4-d^5$  unit built up from octahedrally coordinated metals in orbitally nondegenerate ground states. When the full  $D_{3h}$  symmetry is assumed, the migration of the "extra" electron among the three centers ( $abc$ ) results in three degenerate configurations:

$$(I) = a^5b^4c^4, \quad (II) = a^4b^5c^4, \quad (III) = a^4b^4c^5,$$

which are coupled by the transfer Hamiltonian

$$H_t = \sum_{i,j,m,m'} [t_{mm'} C_{m\sigma}^*(i) C_{m'\sigma}(j)],$$

where  $t_{mm'}$  deals with the transfer integral between the orbitals  $m$  and  $m'$ , and  $C_{m\sigma}^*$  ( $C_{m'\sigma}$ ) creates (annihilates) the electron of spin  $\sigma$  located at  $m$  ( $m'$ ). Then, the product  $C_{m\sigma}^*(i) C_{m'\sigma}(j)$  represents the transfer of one electron from the orbital  $m'$  of site  $j$  to the orbital  $m$  of site  $i$ , keeping the spin state unchanged. In order to reduce the number of parameters, an averaged transfer integral,  $t$ , is assumed. This hamiltonian gives off-diagonal elements in the matrix representation. A further term to be considered is the Heisenberg exchange coupling between the three sites, which can be described by the well-known Hamiltonian

$$H_{ex} = \sum_{i < j} J_{ij} S_i S_j,$$

where  $J_{ij}$  deals with the "static" exchange constant between sites  $i$  and  $j$ . In the case under consideration, two distinct exchange parameters need to be considered, namely  $J$  for the  $Mn^{II}-Mn^{III}$  interactions, and  $J'$  for the  $Mn^{III}-Mn^{III}$  interaction.

The above discussion deals with an equilateral triangle ( $D_{3h}$  symmetry). Under such an assumption, the energy levels of the entity are determined by three parameters: the transfer parameter,  $t$ , and the two exchange parameters,  $J$  and  $J'$ . The introduction of an asymmetry in the triangle (site  $a$  being different from  $b$  and  $c$ , for example) gives rise to a trapping effect with the extra electron showing a preference to be on site  $a$ . This results in the stabilization of the configuration (I) with respect to the other two, by an energy  $-U$ . On the other hand, such an asymmetry may lead to different overlapping of wave functions of metal ions and hence, two different transfer integrals, namely  $t$  and  $t'$ , need to be accounted.

**MAGNETIC BEHAVIOR OF THE MIXED-VALENCE UNIT**  
 $d^4-d^4-d^5$

First, let us examine the influence of the electronic transfer on the energy spectra and magnetic properties. Depending on the ratio between the two transfer integrals considered, we find two extreme situations: the linear trimer (in the case  $t'/t = 0$ ) and the equilateral triangle ( $t'/t = 1$ ). We notice that for a linear trimer, the transfer stabilizes the ferromagnetic ground state  $S = 13/2$ ; consequently, the product  $\chi T$  increases upon cooling down (Fig. 1). This result is in agreement with the tendency of a delocalized electron to give a parallel spin alignment, according to a double exchange mechanism. As the ratio  $t'/t$  increases, the energy of the ground state approaches to the energies of excited states, and finally, for the equilateral triangle ( $t'/t = 1$ ), the ground state becomes a spin mixture containing states with  $S$  ranging from  $1/2$  to  $13/2$ . This accidental degeneracy of levels gives rise to a paramagnetic behavior of the system, with  $\chi T$  staying nearly constant. This result shows that the consideration only of the transfer is insufficient to explain the antiferromagnetic behavior observed in mixed-valence trinuclear manganese complexes.<sup>7</sup> Thus, other factors such as the magnetic exchange should also be accounted for.

In examining the influence of the magnetic exchange, we focus on the equilateral unit. Dealing with the energy spectra, it is worth noticing that the splitting of the levels under the influence of a magnetic exchange depends only on the total spin  $S$ . That means that for  $t \gg J$ , the splitting of the degenerate ground state (separated from the first excited state by an energy  $0.4t$ ) gives the same energy diagram as the trapped trimer ( $t = 0$ ), with a doubly degenerated ground state  $S = 1/2$ , and similar degeneracies for the excited states (Fig. 2). Consequently, very close magnetic behaviors are predicted, irrespective of the valence delocalization. The only effect of the electronic transfer on the magnetic properties is a weak enhancement of the magnetic moment as the temperature is increased, due to the population of the levels with  $S > 5/2$ , which are more degenerated. In the limit of high temperatures, that gives a magnetic moment 16% higher for the fully delocalized trimer (Fig. 3).

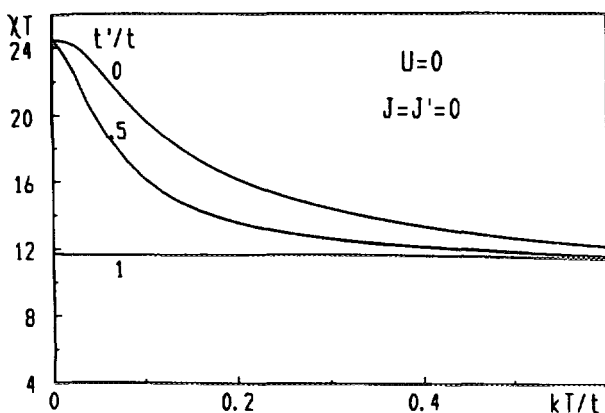


FIG. 1. Theoretical variation of the product  $\chi T$  vs  $kT/t$  showing the influence of the relative electronic transfers ( $t'/t$ ).

S	(1)	E	S	(2)	E
13/2	(1)	-14 J	13/2	(2)	-t - 14 J
11/2	(2)	-7.5 J	11/2	(3)	-t - 7.5 J
9/2	(3)	-2 J	9/2	(4)	-t - 2 J
7/2	(4)	2.5 J	7/2	(5)	-t + 2.5 J
5/2	(5)	6 J	5/2	(6)	-t + 6 J
3/2	(4)	8.5 J	3/2	(4)	-t + 8.5 J
1/2	(2)	10 J	1/2	(2)	-t + 10 J
		$J = J'$			$J = J'$
		$t = t' = 0$			$t = t' = 100  J $

FIG. 2. Equilateral triangle. Spectrum and degeneracies of the low lying states for valence-trapped ( $t = 0$ ) and delocalized ( $t \gg J$ ) limits showing the influence of a Heisenberg exchange interaction.

Finally, the influence of the trapping parameter  $U$  on the energy levels is to stabilize the state of highest multiplicity. This is similar to the result obtained in the linear trimer when a transfer is considered.

The above results differ significantly from those obtained in mixed-valence dimers or linear trimers, in which the transfer stabilizes a ferromagnetic ground state, while exchange and trapping parameters stabilize the antiferromagnetic one, giving rise to energy diagrams very sensitive to the electronic delocalization.<sup>4</sup> Thus, in the triangular mixed-valence system, the effect of the exchange is almost to split the "paramagnetic" ground state generated by the transfer, giving rise to an energy diagram that, in most cases, closely resembles that of the valence-trapped model.

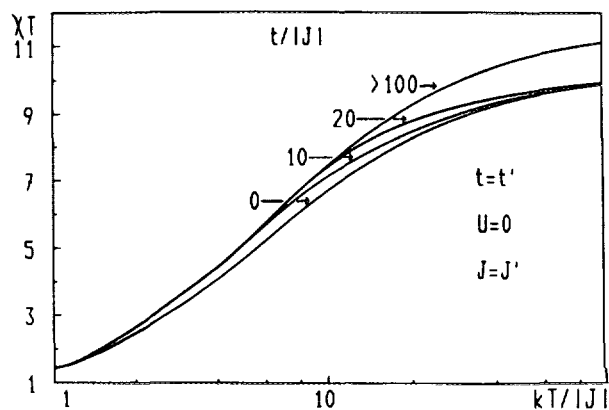


FIG. 3. Magnetic behavior of an antiferromagnetically coupled triangular unit showing the influence of the ratio  $t/|J|$ .

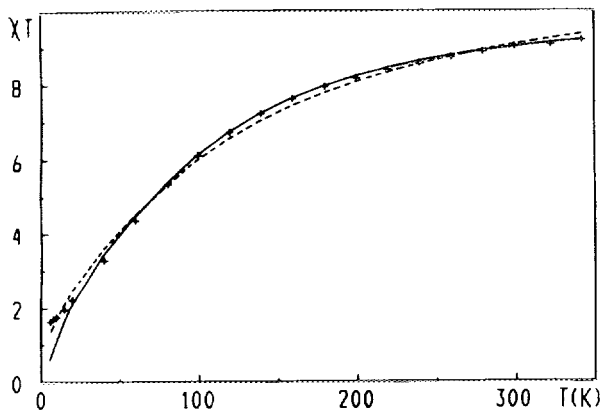


FIG. 4. Experimental (+) and calculated magnetic behaviors for the trimer  $[\text{Mn}_3\text{O}(\text{O}_2\text{CMe})_6(\text{pyr})_3](\text{pyr})$ . Dashed and full lines represent the best fits of the data to the valence-trapped ( $t = 0$ ) (Ref. 7) and delocalized models, respectively.

### THE TRINUCLEAR OXO-CENTERED Mn(II)-Mn(II)-Mn(III) COMPLEXES

These compounds have recently been reported<sup>7</sup> and, in some of them, a rapid electron transfer is predicted in view of the  $D_{3h}$  symmetry of the trinuclear entities. In discussing the magnetic behaviors of these compounds, the electronic transfer has been neglected and a localized Heisenberg model has been used. A satisfying fit of the experimental data has been found. However, the resulting Landé parameters (about 2.1) are larger than expected (lesser than 2). This is quite normal taking into account the results of the valence-delocalized model that, in presence of an electronic transfer, predicts an additional contribution to the magnetic moment (see Fig. 2). In Fig. 4 we have reported the best fit of the

magnetic data to the dynamic model for the trimer  $[\text{Mn}_3\text{O}(\text{O}_2\text{CMe})_6(\text{pyr})_3](\text{pyr})$ . Owing to the structural features of the trimer, in the fitting procedure we have kept  $t = t'$  and  $U = 0$ . The fitting parameters are  $t = 280 \text{ cm}^{-1}$ ,  $J = -10.2 \text{ cm}^{-1}$ ,  $J' = -12.8 \text{ cm}^{-1}$ , and  $g = 2$ . As expected, we notice that the Landé factors are now more realistic. On the other hand, despite the little sensitivity of the susceptibility to the transfer, the dynamic model approaches better the experimental data. This is particularly noticeable in the temperature range 50–200 K. In this, the systematic deviations of the data to the trapped model vanish when an electronic transfer about  $300 \pm 100 \text{ cm}^{-1}$  is considered. Notice that for larger values of  $t$ , the magnetic behaviors are almost identical to that obtained from the trapped model, justifying the validity of the above fit.

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