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Nature of the Interaction between Ln^{III} and Cu^{II} Ions in the Ladder-Type Compounds $\{Ln_2[Cu(opba)]_3\}\cdot S$ (Ln = Lanthanide Element; opba = *ortho*-Phenylenebis(oxamato), S = Solvent Molecules)

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To date, most of the studies dealing with the magnetic properties of 4f−3d compounds have been limited to the case in which the 4f ion was Gd^{III}, with a pure spin ground state. For the lanthanide(III) ions with a first-order orbital momentum, the determination of the nature of the 4f−3d interaction is still a challenge. This paper addresses this problem. The magnetic properties of the compounds of formula $\{Ln_2[M(opba)]_3\}\cdot S$ (abbreviated hereafter as Ln_2M_3) have been investigated; Ln stands for a lanthanide element, M for Cu or Zn, opba for *ortho*-phenylenebis(oxamato), and S for solvent molecules. All of these compounds have similar one-dimensional structures consisting of ladder-type motifs. Our approach consisted of comparing the magnetic properties of Ln_2Cu_3 and Ln_2Zn_3 for each Ln^{III} ion. The former are governed by both the thermal population of the Stark components of Ln^{III} and the $Ln^{III}-Cu^{II}$ interaction; the latter are only governed by the thermal population of the Ln^{III} Stark components. It has been confirmed that the $Gd^{III}-Cu^{II}$ interaction was ferromagnetic, and it was found that the $Tb^{III}-Cu^{II}$ and $Dy^{III}-Cu^{II}$ interactions were ferromagnetic as well. The $Tm^{III}-Cu^{II}$ interaction might also be ferromagnetic; the situation, however, is uncertain. On the other hand, in all other cases the $Ln^{III}-Cu^{II}$ interaction is not ferromagnetic; it is either not detectable by the magnetic technique or antiferromagnetic. The difference between $Dy^{III}-Cu^{II}$ (ferromagnetic) and $Ho^{III}-Cu^{II}$ (not ferromagnetic) is particularly striking. These findings have been discussed.

Introduction

The mechanism of the interaction between two 3d magnetic ions within a polynuclear species is nowadays rather well understood.[1] The factors governing the nature, antiferro- or ferromagnetic, and the magnitude of this interaction can be controlled to some extent, so that it is now possible to design such species that exhibit predictable magnetic properties.[2] Perhaps the most difficult situation is that in which at least one of the two interacting ions possesses a first-order orbital momentum, for instance the Co^{II} ion in octahedral surroundings. In such a case, the Heisenberg−Dirac−Van Vleck phenomenological Hamiltonian is no longer appropriate in describing the spectrum of the low-lying states.[1]

When a lanthanide(III) ion, Ln^{III}, is involved in the interaction, the situation is much less advanced as far as the understanding of the interaction phenomenon is concerned. This is particularly true when Ln^{III} has an orbital contribution. For two decades or so, a large number of compounds containing both lanthanide and transition metal ions have been described.[3] However, most of the magnetic studies were limited to the case in which the Ln^{III} is Gd^{III}, the 3d metal ion usually being Cu^{II}. A noticeable exception is the very recent paper by Costes et al.[4] To the best of our knowledge, the $Gd^{III}-Cu^{II}$ interaction has been found to be ferromagnetic for all investigated compounds, irrespective of the structural details. The same situation was observed for the interaction between Gd^{III} and an organic radical.[5] So far, very little is known concerning the interaction between a Ln^{III} ion with a first-order orbital momentum and Cu^{II}. This paper addresses this problem. To some extent, our approach is similar to that developed by Costes et al. Our conclusions, however, will be significantly different from those drawn by these authors.

The $4f^n$ configuration of a Ln^{III} ion is split into $^{2S+1}L_J$ states by the interelectronic repulsion and the spin−orbit coupling. Each of these states is further split in Stark components (up to $2J+1$ if n is even and $J+{}^1/_2$ if n is odd) due to the crystal field perturbation. The number of Stark components depends on the site symmetry of the ion.[6] For all the magnetic Ln^{III} ions, except Sm^{III}, the $^{2S+1}L_J$ ground state is well-separated in energy from the first excited states. At room temperature, all the Stark components arising from this ground state are populated. A progressive depopulation of the excited Stark components occurs as the temperature is lowered. For a mononuclear species

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containing a Ln^{III} ion with a first-order orbital momentum, this temperature dependence of the population of the Stark components leads to a deviation of the magnetic susceptibility with respect to the Curie law. $\chi_M T$ (χ_M being the molar magnetic susceptibility and T the temperature) is not constant as a function of the temperature. When the Ln^{III} ion is exchange-coupled with a 3d magnetic ion, for instance Cu^{II}, the temperature dependence of $\chi_M T$ is due to both the thermal population of the Ln^{III} Stark components and the $Ln^{III}-Cu^{II}$ coupling. It follows that it is, in principle, very difficult to determine not only the magnitude of the $Ln^{III}-Cu^{II}$ interaction, but even its nature. This situation explains why to date only the 4f−3d systems, in which the lanthanide ion is Gd^{III}, have been considered.

Our approach in obtaining new insights on the nature of the $Ln^{III}-Cu^{II}$ interaction with other magnetic lanthanide ions consists of comparing the magnetic properties of isostructural $Ln^{III}Cu^{II}$ and $Ln^{III}Zn^{II}$ compounds. The Zn^{II} ion in the latter compound is obviously diamagnetic, and the deviation of the magnetic susceptibility of this compound with respect to the Curie law is due entirely to the thermal population of the Ln^{III} Stark components. Transferring this information into the magnetic properties of the $Ln^{III}Cu^{II}$ compound may result in the determination of the nature of the $Ln^{III}-Cu^{II}$ interaction.

We have reported on several families of one- and two-dimensional compounds involving both Ln^{III} and Cu^{II} ions that were synthesized from the $[Cu(pba)]^{2-}$ and $[Cu(opba)]^{2-}$ precursors; pba stands for propylenebis(oxamato) and opba for *ortho*-phenylenebis(oxamato).[7] The compounds of one of these families have the formula $\{Ln_2[Cu(opba)]_3\}\bullet S$ where S stands for solvent molecules. When S is DMSO, the compounds have a ladder-type structure and are isostructural over the whole lanthanide series. This situation is particularly interesting because it allows us to compare the magnetic properties as the lanthanide element Ln varies along the series in structurally related compounds.

In a preceding paper, it has been shown through WAXS (wide-angle X-ray scattering) experiments that the $\{Ln_2[Cu(opba)]_3\}\cdot S$ and $\{Ln_2[Zn(opba)]_3\}\cdot S$ compounds, hereafter abbreviated as Ln_2Cu_3 and Ln_2Zn_3, respectively, have very similar structures.[8] These structures consist of discrete, infinite ladder-type motifs as shown in Figure 1. The sidepieces of the ladders are made of Ln[M(opba)] units, with M = Cu or Zn, and the rungs are made of [M(opba)] units that bridge two Ln atoms belonging to either sidepiece of the ladder. When seen along the direction of a rung, the two edges of a ladder are in an eclipsed conformation. Each Ln^{III} ion is surrounded by three $[M(opba)]^{2-}$ groups, its coordination sphere being completed by solvent molecules. The Ln-M separations across the oxamato bridge range from 5.60 to 6.45 Å, and the separation between two Ln^{III} ions connected in the transverse direction ranges from 11.15 to 11.75 Å, depending on the nature of the Ln^{III} and M^{II} ions. The packing distance between two ladders ranges from 9.0 to 9.5 Å.[8]

Experimental Section

Syntheses. All compounds were obtained according to the procedures described in ref 8.

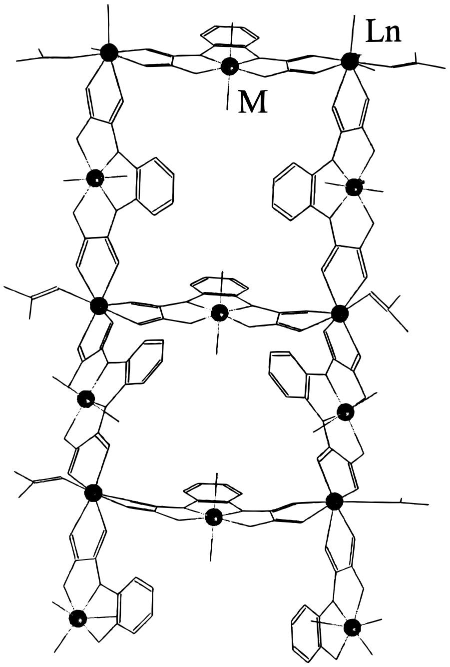

Figure 1. View of the structural model for $\{Ln_2[M(opba)]_3\}\cdot S$ deduced from WAXS studies.

Magnetic Measurements. These were carried out with a Quantum Design MPMS-5S SQUID magnetometer working in the dc mode. The measurements were performed in the 2−300 K temperature range, with a magnetic field of 10^3 Oe. Diamagnetic corrections of the constituent atoms were estimated from Pascal's constants as -291×10^{-6} emu mol^{-1}.[9] All the compounds are highly solvated with dimethylsulfoxide and water molecules, and the exact number of noncoordinated solvent molecules is not known accurately. Some of these molecules are easily removed. Therefore, there is some uncertainty in the molecular weight of the compounds and consequently in the molar magnetic susceptibilities. To overcome this difficulty, it was assumed that for each compound the high-temperature limit of $\chi_M T$ was reached at 300 K, and the experimental $\chi_M T$ values were rescaled accordingly when necessary. In the particular case of Ln = Sm, the treatment was different. Indeed, the magnetic measurements exhibit a component due to the thermal population of the first excited state, $^6H_{7/2}$. This component was first subtracted before scaling the high-temperature limit of $\chi_M T$.

Results

The $Gd^{III}-Cu^{II}$ Case. Let us make clear our approach in the simple case of the $Gd^{III}-Cu^{II}$ interaction in Gd_2Cu_3. Gd^{III} has an $^8S_{7/2}$ ground state without first-order orbital momentum. There is a unique Stark component. Within the ladder structure, the interaction between two nearest neighbor Gd^{III} ions, separated by more than 10 Å, is certainly negligibly small compared to the $Gd^{III}-Cu^{II}$ interaction through the oxamato bridge. Therefore, the magnetic behavior of Gd_2Zn_3 is expected to follow the Curie law that is anticipated for two isolated Gd^{III} ions. Such a Curie law is observed down to 9 K, with $\chi_M T$ constant and equal to 15.7 emu K mol^{-1}. As T is lowered further below 9 K, $\chi_M T$ decreases very slightly and reaches 14.8 emu K mol^{-1} at 2 K, which might be due to interladder effects. Let us note that the intra- and/or interladder interactions in La_2Cu_3 involving the diamagnetic La^{III} ion are also very weak; $\chi_M T$ for this compound is constant and equal to 1.13 emu K mol^{-1} down to about 6 K, then diminishes down to 1.05 emu K mol^{-1} as T is lowered from 6 to 2 K. For Gd_2Cu_3, the deviation of the magnetic behavior with respect to the Curie law will be due

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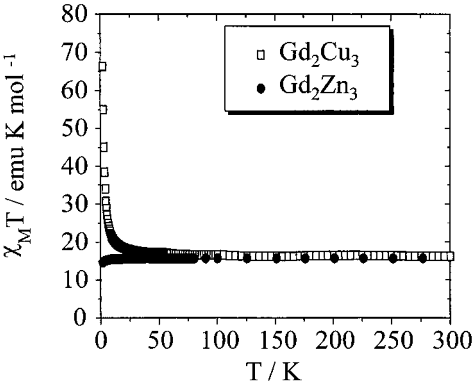

Figure 2. $\chi_M T$ versus T curves for Gd_2Cu_3 (□) and Gd_2Zn_3 (●) compounds.

essentially to the $Gd^{III}-Cu^{II}$ interaction. $\chi_M T$ for this compound is constant and equal to 16.9 emu K mol^{-1} down to 50 K, then increases more and more rapidly as T is lowered further, reaching 66 emu K mol^{-1} at 2 K. The $\chi_M T$ versus T plots for Gd_2Cu_3 and Gd_2Zn_3 are compared in Figure 2. This comparison clearly reveals the ferromagnetic nature of the $Gd^{III}-Cu^{II}$ interaction. This result was already well established, and actually Gd_2Cu_3 has been found to exhibit a long-range ferromagnetic ordering at a T_c of 1.75 K.[10] It is also interesting to consider the temperature dependence of the difference of magnetic susceptibilities: $\Delta = (\chi_M T)_{Gd_2Cu_3} - (\chi_M T)_{Gd_2Zn_3}$. Δ is constant and equal to 1.1 emu K mol^{-1} down to 50 K, which corresponds to the contribution of three isolated Cu^{II} ions, then increases very rapidly as T is lowered. This profile for Δ is characteristic of ferromagnetic correlations within the compound.

The $Dy^{III}-Cu^{II}$ and $Tb^{III}-Cu^{II}$ Cases. Let us now consider the $Dy^{III}-Cu^{II}$ interaction in Dy_2Cu_3. Dy^{III} has a $^6H_{15/2}$ ground state, with a first-order orbital momentum. In the low symmetry site, this state is split into eight Stark components by the crystal field, each of them being a Kramers doublet. The energy gap between highest and lowest Kramers doublets is on the order of a few hundreds of wavenumbers. As the temperature is lowered, the highest Kramers doublets are progressively depopulated, and at 2 K only the ground Kramers doublet is populated. This thermal (de)population leads to a pronounced deviation of the magnetic behavior of Dy_2Zn_3 with respect to the Curie law. $\chi_M T$ is equal to 28.3 emu K mol^{-1} at 300 K and decreases more and more rapidly as T approaches absolute zero. The $\chi_M T$ value at 2 K is 21.1 emu K mol^{-1}. For Dy_2Cu_3, $\chi_M T$ is equal to 29.4 emu K mol^{-1} at room temperature, then decreases as T is lowered down to 14 K. It reaches a minimum at that temperature, with $\chi_M T = 26.6$ emu K mol^{-1}, then increases dramatically as T approaches to zero. The two $\chi_M T$ versus T plots are compared in Figure 3. This comparison clearly shows that the decrease of $\chi_M T$ down to 14 K for Dy_2Cu_3 arises from the depopulation of the excited Stark components of Dy^{III}. This is a local effect, which is also observed for Dy_2Zn_3. On the other hand, the magnetic behavior of Dy_2Cu_3 below 14 K is dominated by the interaction between Dy^{III} and Cu^{II}, both in their local ground Kramers doublet state. This interaction is ferromagnetic. This situation is emphasized by the temperature dependence of the difference, $\Delta = (\chi_M T)_{Dy_2Cu_3} - (\chi_M T)_{Dy_2Zn_3}$ also represented in Figure 3. Δ is constant and equal to 1.1 emu K mol^{-1} from 300 down to about 100 K, which corresponds to the contribution of three isolated Cu^{II} ions, then increases more and more rapidly as T approaches to zero. As for the preceding case, this profile is characteristic of ferromagnetic correlations.

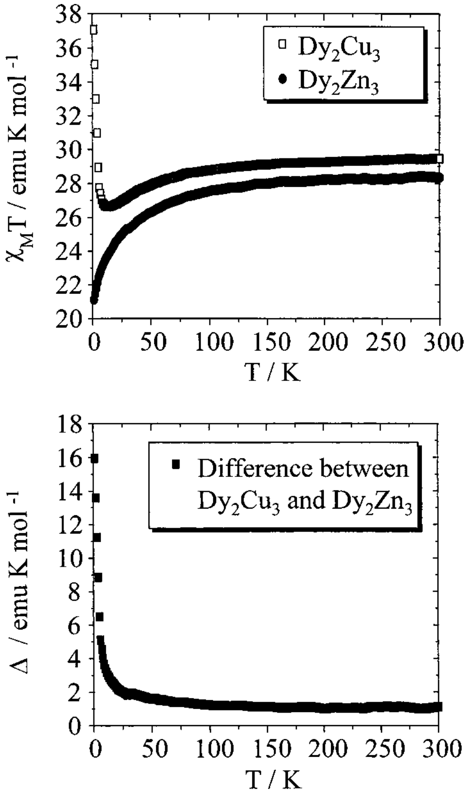

Figure 3. (top) $\chi_M T$ versus T curves for Dy_2Cu_3 (□) and Dy_2Zn_3 (●) compounds. (bottom) $\Delta = (\chi_M T)_{Dy_2Cu_3} - (\chi_M T)_{Dy_2Zn_3}$ versus T curve (see text).

The $\chi_M T$ versus T plots for Tb_2Cu_3 and Tb_2Zn_3 are compared in Figure 4. The behavior is qualitatively similar to that observed for the $Dy_2Cu_3 - Dy_2Zn_3$ couple. The decrease of $\chi_M T$ for Tb_2Cu_3 as T is lowered from 300 down to 20 K is due to depopulation of the excited Stark components of Tb^{III}, whereas the increase of $\chi_M T$ as T is lowered further is due to ferromagnetic correlations between the Tb^{III} and Cu^{II} magnetic moments.

The $Tm^{III}-Cu^{II}$ Case. The $\chi_M T$ versus T plots for Tm_2Cu_3 and Tm_2Zn_3 are compared in Figure 5. For both compounds, $\chi_M T$ is first constant as T is lowered, then decreases. Therefore, the situation is not the same as for the previous cases, and it is difficult to conclude as to the nature of the $Tm^{III}-Cu^{II}$ interaction. The temperature dependence of the difference, $\Delta = (\chi_M T)_{Tm_2Cu_3} - (\chi_M T)_{Tm_2Zn_3}$, is also shown in Figure 5. Δ increases as T is lowered in the low-temperature range. This might suggest that ferromagnetic correlations are again present in Tm_2Cu_3. The increase of Δ from about 50 K down to 2 K might also be due to the fact that the relative energies of the Stark components of Tm^{III} are not strictly the same in Tm_2Cu_3 and Tm_2Zn_3. Our conclusion is that it is not possible to assert that Tm_2Cu_3 present ferromagnetic correlations.

Other $Ln^{III}-Cu^{II}$ Cases, with Ln = Ce, Pr, Nd, Sm, Ho, Er, and Yb. We will restrict ourselves to a typical example, that of Ln = Ho. The $\chi_M T$ versus T curves for Ho_2Cu_3 and Ho_2Zn_3 are compared in Figure 6. These two curves are very similar, with $\chi_M T$ decreasing continuously as T is lowered. The thermal population of the Stark components of Ho^{III} dominates the magnetic properties of Ho_2Cu_3. The temperature dependence of the difference $\Delta = (\chi_M T)_{Ho_2Cu_3} - (\chi_M T)_{Ho_2Zn_3}$ is also shown in Figure 6. Δ is rather constant and equal to 1 emu K mol^{-1} from 300 down to about 60 K. This difference corresponds to

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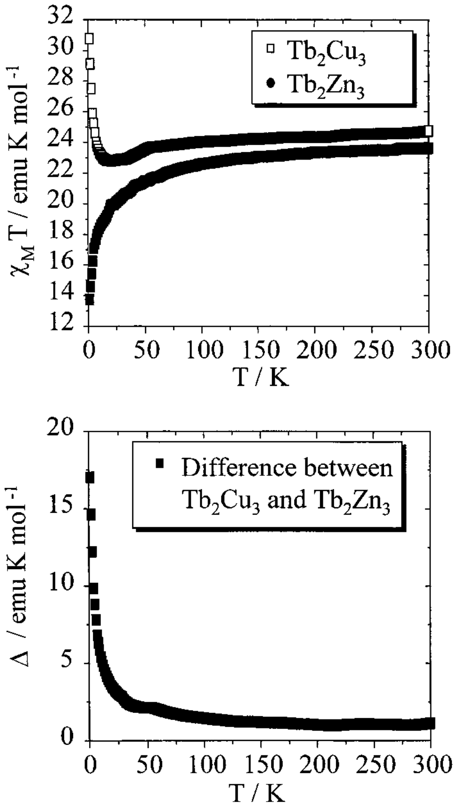

Figure 4. (top) $\chi_M T$ versus T curves for Tb_2Cu_3 (□) and Tb_2Zn_3 (●) compounds. (bottom) $\Delta = (\chi_M T)_{Tb_2Cu_3} - (\chi_M T)_{Tb_2Zn_3}$ versus T curve (see text).

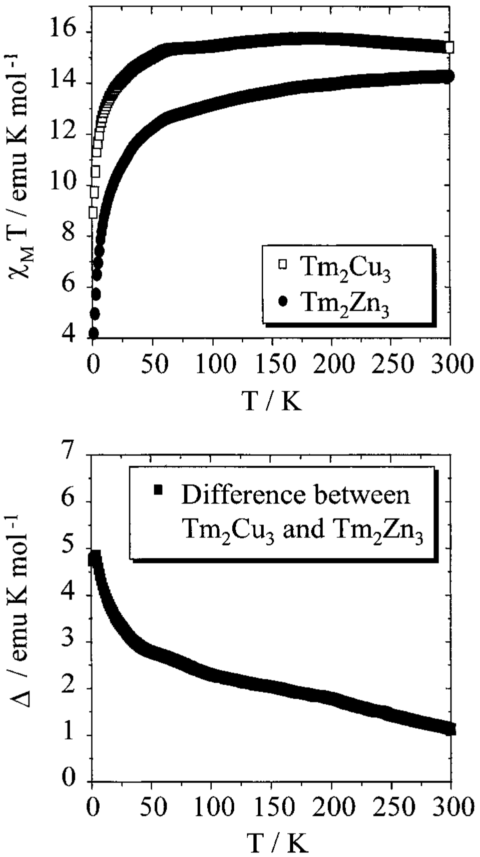

Figure 5. (top) $\chi_M T$ versus T curves for Tm_2Cu_3 (□) and Tm_2Zn_3 (●) compounds. (bottom) $\Delta = (\chi_M T)_{Tm_2Cu_3} - (\chi_M T)_{Tm_2Zn_3}$ versus T curve (see text).

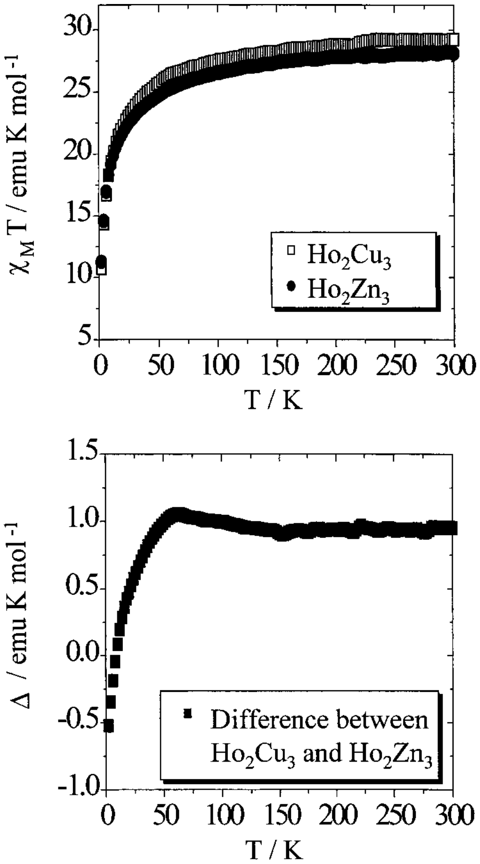

Figure 6. (top) $\chi_M T$ versus T curves for Ho_2Cu_3 (□) and Ho_2Zn_3 (●) compounds. (bottom) $\Delta = (\chi_M T)_{Ho_2Cu_3} - (\chi_M T)_{Ho_2Zn_3}$ versus T curve (see text).

the contribution of three isolated Cu^{II} ions. Then, Δ decreases as T is lowered further. At 2 K, Ho_2Cu_3 is less magnetic than Ho_2Zn_3; Δ is negative (− 0.6 emu K mol^{-1}). The profile of this Δ versus T curve contrasts with what has been described above. No ferromagnetic correlation is detected. The interaction between Ho^{III} and Cu^{II} in their local ground states, if any, might be antiferromagnetic. The same conclusion can be drawn with Ln = Ce, Pr, Nd, Sm, Er, and Yb.

Discussion

This work demonstrates that the $Ln^{III}-Cu^{II}$ interaction is ferromagnetic, not only for Ln = Gd but also for Ln = Tb and Dy. Perhaps the $Tm^{III}-Cu^{II}$ interaction is ferromagnetic as well. However, it is not possible to conclude unambiguously in this case. On the other hand, for all the other magnetic Ln^{III} ions, the $Ln^{III}-Cu^{II}$ interaction is not ferromagnetic.

The approach we used to reach this conclusion was to compare the magnetic properties of isostructural $Ln^{III}Cu^{II}$ and $Ln^{III}Zn^{II}$ compounds. For a $Ln^{III}Cu^{II}$ compound, the temperature dependence of the magnetic susceptibility is governed by two factors, namely, the energy spectrum of the Stark components of Ln^{III} and the $Ln^{III}-Cu^{II}$ interaction. The former factor is local, and the latter is associated with the pair of interacting spin carriers. Knowledge of the magnetic properties of the isostructural $Ln^{III}Zn^{II}$ species may allow us to characterize semiquantitatively the local factor and, therefore, to extract the interaction factor from the magnetic data for the $Ln^{III}Cu^{II}$ compound.

At this stage, it is important to stress that we are dealing with extended compounds, which makes our approach more reliable. As a matter of fact, for an extended compound with a

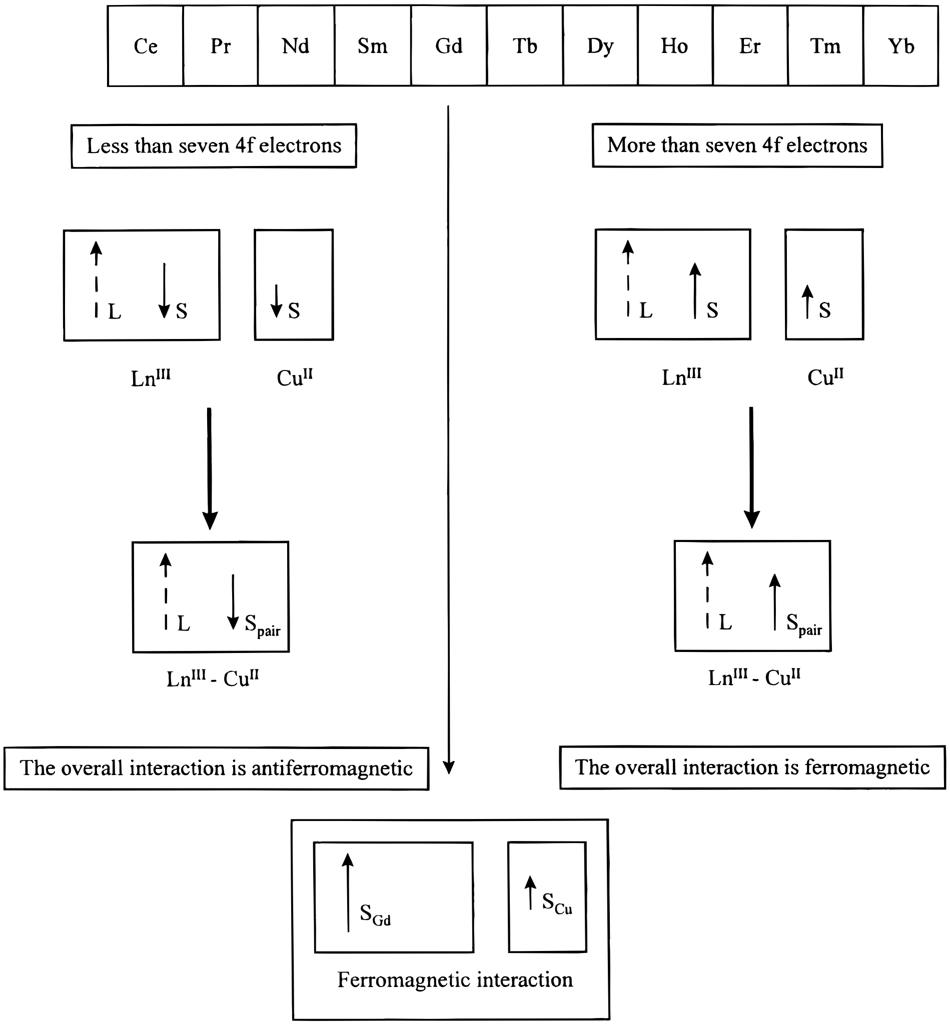

Figure 7. Schematic representation of the angular momentum coupling in a $Ln^{III}-Cu^{II}$ pair, where Ln^{III} is a trivalent lanthanide ion carrying an orbital momentum.

ferromagnetic $Ln^{III}-Cu^{II}$ interaction, the correlation length along which the Ln^{III} and Cu^{II} magnetic moments align in a parallel fashion becomes infinite as T approaches absolute zero (or the critical temperature of the compound), and $\chi_M T$ tends to very high values. In other words, the effect of ferromagnetic correlations overcomes the effect of depopulation of the Stark components of Ln^{III}. If we were dealing with a ferromagnetically coupled $Ln^{III}Cu^{II}$ binuclear compound, the low-temperature limit of $\chi_M T$ would be much lower, and the interaction effect might not overcome the Ln^{III} local effect. For a $Gd^{III}Cu^{II}$ pair with a $S = 4$ ground state and a $S = 3$ low-lying excited state $\chi_M T$ increases as T decreases; however, the ratio between low- and high-temperature limits of $\chi_M T$ is only 1.21 (assuming that the local *g*-factors for Gd^{III} and Cu^{II} are equal). For a ferromagnetically coupled $Dy^{III}Cu^{II}$ pair, the increase of $\chi_M T$ due to the interaction may be hidden by the decrease due to the Ln^{III} crystal field effect. Such a situation has been observed in a tetranuclear species in which a central Dy^{III} ion interacts with three peripheral Cu^{II} ions.[11]

Let us come back to the Tb_2Cu_3 and Dy_2Cu_3 compounds. In both cases, the $\chi_M T$ versus T curve exhibits a rounded minimum at 22 and 12 K, respectively. Such a profile is quite reminiscent of what is expected and observed for ferrimagnetic compounds, with a $Ln^{III}-Cu^{II}$ antiferromagnetic interaction and noncompensation of the two spin sublattices. The divergence of $\chi_M T$ in the low-temperature range would then be attributed to the fact that the correlation length along which the Ln^{III} and Cu^{II} magnetic moments align in an antiparallel fashion would approach the infinite. Such a conclusion would be erroneous. The minima in the $\chi_M T$ versus T curves result from the antagonist effects of ferromagnetic correlations and Ln^{III} crystal field splittings. Let us try to compare the strength of the ferromagnetic interactions for $Gd^{III}-Cu^{II}$, $Tb^{III}-Cu^{II}$, and $Dy^{IIII}-Cu^{II}$. The idea is that the larger this strength is, the higher the difference, $\Delta = (\chi_M T)_{Ln_2Cu_3} - (\chi_M T)_{Ln_2Zn_3}$, at the lowest temperature reached, that is 2 K. Δ is equal to 54 emu K mol^{-1} when Ln^{III} is Gd^{III}, only 17 emu K mol^{-1} when Ln^{III} is Tb^{III}, and 16 emu K mol^{-1} when Ln^{III} is Dy^{III}. Therefore, we can suggest that the compound Gd_2Cu_3 presents the strongest ferromagnetic interactions. This assertion is in line with the fact that this compound exhibits a long-range ferromagnetic ordering, which is not observed for Tb_2Cu_3 and Dy_2Cu_3.

For all the Ln^{III} ions except Gd^{III}, Tb^{III} and Dy^{III}, the $Ln^{III}-Cu^{II}$ interaction is clearly not ferromagnetic. The difference $\Delta = (\chi_M T)_{Ln_2Cu_3} - (\chi_M T)_{Ln_2Zn_3}$ decreases as T decreases and becomes negative at very low temperature. Such a behavior precludes a significant $Ln^{III}-Cu^{II}$ antiferromagnetic interaction as well. As a matter of fact, if this were so, Ln_2Cu_3 would be a ferrimagnet with a minimum in the $\chi_M T$ versus T curve occurring above 2 K and a divergence of $\chi_M T$ as T approaches

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absolute zero. Therefore, Δ would also diverge at low temperature. Actually, the minimum of $\chi_M T$ for Ln_2Cu_3, if any, occurs below 2 K, and the interaction is very weak. To sum up this discussion concerning the Ln^{III} ions other than Gd^{III}, Tb^{III} and Dy^{III}, we prefer to say that the $Ln^{III}-Cu^{II}$ ineraction is probably negligibly small. In one exceptional case, however, a rather large antiferromagnetic interaction might be compatible with the experimental data. This would happen if the two antiferromagnetically coupled spin sublattices would compensate accidentally. The ground state would then be (quasi) nonmagnetic. Such a situation has been reported for $Nd_2[Cu(pba)]_3 \cdot 23H_2O$ and might occur as well for $\{Nd_2[Cu(opba)]_3 \cdot S$.[12]

The last but not the least question we are faced with is the interpretation of the results. Why is the $Ln^{III}-Cu^{II}$ interaction ferromagnetic (F) when Ln is Gd, Tb and Dy (and perhaps also Tm) and not detectable or antiferromagnetic (AF) for the other Ln^{III} ions ? A few years ago, one of us suggested a very simple and rather naive mechanism, according to which the $Ln^{III}-Cu^{II}$ interaction was expected to be AF for the Ln^{III} ions with less than seven 4f electrons and F otherwise.[13] Let us briefly review the arguments justifying this prediction. The $Gd^{III}-Cu^{II}$ interaction is F, whatever the structure of the compound. This was attributed to the coupling between the $4f^7$-$3d^9$ ground configuration and the $4f^75d^1$-$3d^8$ excited configuration, in which an electron has been transferred from the singly occupied 3d orbital of Cu^{II} to the empty 5d orbitals of Gd^{III}. It was assumed that this mechanism remained valid for the other magnetic Ln^{III} ions, leading to an F coupling between the Ln^{III} and Cu^{II} spins. When the number of 4f electrons is less than seven, the orbital and spin momenta of Ln^{III} are antiparallel, and the F spin coupling gives rise to an overall AF interaction between angular momenta. When the number of 4f electrons is more than seven, the orbital and spin momenta of Ln^{III} are parallel, and the F spin coupling gives rise to an overall F interaction. This mechanism is schematized in Figure 7. The results presented in this paper are not in line with this mechanism. If the $Ln^{III}-Cu^{II}$ interaction is F for Gd^{III} ($4f^7$), Tb^{III} ($4f^8$), and Dy^{III} ($4f^9$), it is not F anymore for Ho^{III} ($4f^{10}$). The difference between Dy^{III} and Ho^{III} is particularly intriguing, and we have no interpretation to put forward yet. Costes et al. reported that the $Ln^{III}-Cu^{II}$ interaction was F for all the heavy Ln^{III} ions, starting from Gd^{III}, except for Tm^{III} and Yb^{III}.[4] There is clearly an opposition between the two studies concerning the $Ho^{III}-Cu^{II}$ and $Er^{III}-Cu^{II}$ cases. This opposition might be due to the fact that the bridges through which the interaction is propagated are not the same. In Costes' compounds, the magnetic ions are bridged by phenolato oxygen atoms, and in our compounds, they are bridged by an oxamato. The opposition may also be due to the fact that Costes' conclusions were drawn from magnetic susceptibility data obtained on binuclear compounds. As already emphasized, it is then much more difficult to discriminate between magnetic interaction and local crystal field effects. The crucial point is that for a $(Ln^{III}$-$Cu^{II})_n$ molecular species, where n is the number of repeat units within the molecule, the influence of the interaction effect on the $\chi_M T$ versus T curve (χ_M being the molar magnetic susceptibility per repeat unit) is roughly proportional to n, whereas the influence of the crystal effect is independent of n.

Conclusion

The main finding of this work concerns the ferromagnetic nature of the $Tb^{III}-Cu^{II}$ and $Dy^{III}-Cu^{II}$ interactions together with the break in the lanthanide series between Dy^{III} and Ho^{III}; the $Ho^{III}-Cu^{II}$ interaction is not ferromagnetic. We have not checked yet whether this result remained valid irrespective of the structural details of the compounds.

A decade ago, Gatteschi and coworkers reported for the first time that the $Gd^{III}-Cu^{II}$ interaction was ferromagnetic.[14] This surprising result was subsequently confirmed by quite a few authors, and some $Gd^{III}Cu^{II}$ molecular materials exhibiting a long-range ferromagnetic ordering were discovered. A further step has been made; the same situation holds for $Tb^{III}-Cu^{II}$ and $Dy^{III}-Cu^{II}$ but not for the other $Ln^{III}-Cu^{II}$ pairs. An uncertainty remains for $Tm^{III}-Cu^{II}$. The microscopic mechanisms leading to such a situation are still obscure. We would like to bring some new insights on these mechanisms in the near future.

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