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Size Effect on Local Magnetic Moments in Ferrimagnetic Molecular Complexes: An XMCD Investigation

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Summary. Molecular chemistry allows to synthesize new magnetic systems with controlled properties such as size, magnetization or anisotropy. The theoretical study of the magnetic properties of small molecules (from 2 to 10 metallic cations per molecule) predicts that the magnetization at saturation of each ion does not reach the expected value for uncoupled ions when the magnetic interaction is antiferromagnetic. The quantum origin of this effect is due to the linear combination of several spin states building the wave function of the ground state and clusters of finite size and of finite spin value exhibit this property. When single crystals are available, spin densities on each atom can be experimentally given by Polarized Neutron Diffraction (PND) experiments. In the case of bimetallic MnCu powdered samples, we will show that X-ray Magnetic Circular Dichroism (XMCD) spectroscopy can be used to follow the evolution of the spin distribution on the Mn^{II} and Cu^{II} sites when passing from a dinuclear MnCu unit to a one dimensional $(MnCu)_n$ compound.

Keywords. X-ray absorption spectroscopy (XAS); XMCD; Quantum size effect.

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Introduction

Molecular magnetism appears as one of the most fruitful area of research in the study of new effects such as the now famous quantum tunneling effect of Mn_{12} compounds [1]. This improvement is mainly due to the flexibility of molecular chemistry that is able to confer original properties to various new objects. In this research area, for many molecular prospects, having the most precise description of the ground state of the molecular species is crucial for the understanding of the magnetic macroscopic properties. This description is provided by the spin density map generally obtained from Polarized Neutron Diffraction (PND) experiments. But this spectroscopy is limited to samples for which large single crystals can be obtained. The goal of our work is to show that X-ray Magnetic Circular Dichroism (XMCD) spectroscopy, for which no single crystals are necessary, can also get unique information on the spin distribution in such molecular systems.

We choose to report here the theoretical and experimental study of a quantum size effect of local magnetization loss that affects finite magnetic clusters presenting open shell transition metal ions in antiferromagnetic exchange interaction. In such systems, whereas the macroscopic magnetization reaches the expected value at saturation, spin Hamiltonian calculations predict that the magnetization of each cation is lower at saturation than the one of the corresponding free ion [2]. This effect has been recently evidenced by *Kahn* [3] by performing PND experiments on two systems:

(i) the one-dimensional MnCu(1,3-propylenebis(oxamato))$(H_2O)_3 \cdot 2H_2O$ [4] $[(MnCu)_n]$ ferrimagnetic chain where no local magnetization loss is expected;
(ii) the $[Mn^{II}((\pm)$-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) Cu^{II}(*N*,*N*′-bis(3-aminopropyl)oxamido)] $(CF_3SO_3)_2$ [5] [MnCu] dinuclear compound for which spin Hamiltonian calculations predict such an effect.

We will first focus on the origin of this quantum size effect. Then, we will briefly introduce the principle of XMCD spectroscopy. The X-ray absorption and XMCD spectra obtained at the Cu and Mn $L_{2,3}$-edges for the two previously described compounds will be presented and analyzed. Finally, we will show that XMCD can be used for powdered samples, as PND for single crystals, to follow the evolution of the spin distribution on the Mn^{II} and Cu^{II} sites when passing from a dinuclear MnCu unit to a one dimensional $(MnCu)_n$ compound.

Results and Discussion

Quantum Size Effect

The quantum size effect of local magnetization loss is evidently not restricted to the bimetallic systems composed of Mn^{II} and Cu^{II} ions. But in order to simplify the explanation of this phenomenon, we will consider an hypothetical system composed of two spins, S_A and S_B, antiferromagnetically coupled with $S_A = 5/2$ and $S_B = 1/2$ (in $\hbar$ units). The Hamiltonian operator $\hat{\boldsymbol{H}}_{\boldsymbol{ham}}$ describing this system is composed of two terms: the first one is the phenomenological *Heisenberg* Hamiltonian and the second one corresponds to the *Zeeman* effect. Therefore, if we assume that

$g = g_{Mn} = g_{Cu} = 2$, it can be written as follows:

$$\hat{\boldsymbol{H}}_{\boldsymbol{ham}} = -J\hat{\mathbf{S}}_{\mathbf{A}} \cdot \hat{\mathbf{S}}_{\mathbf{B}} + g\mu_B \hat{\mathbf{H}} \cdot \hat{\mathbf{S}}$$

Where $\hat{\mathbf{S}}_{\mathbf{A}}$ and $\hat{\mathbf{S}}_{\mathbf{B}}$ are the spin operators related to S_A and S_B, $\hat{\mathbf{S}} = \hat{\mathbf{S}}_{\mathbf{A}} + \hat{\mathbf{S}}_{\mathbf{B}}$, J is the exchange constant, $\hat{\mathbf{H}}$ the applied magnetic field and μ_B stands for *Bohr* magneton.

If we suppose an antiferromagnetic interaction between S_A and S_B, the ground state in the presence of a magnetic field can be written as $|(S_A = 5/2,\ S_B = 1/2),\ S = 2, Ms = -2>$. When the magnetic saturation is reached, this ground state is the only one populated and one can neglect the contribution of the excited spin states. Since we also neglect in this model any orbital contribution to magnetic moments, the value of the magnetization at saturation, M_{Sat}, of such a system is $2\,g\,\mu_B = 4\,\mu_B$. This value is the one that is expected and experimentally observed for such complexes [6].

This ground state is an eigenfunction of $\hat{\mathbf{S}}_{\mathbf{z}}$, the projection of $\hat{\mathbf{S}}$ on the quantification axis. But if we are interested in the local magnetic moments carried by the Mn^{II} ($S_{Mn} = 5/2$) and Cu^{II} ($S_{Cu} = 1/2$) cations, the adequate quantum numbers are M_{SMn} and $M_{SCu,}$ respectively eigenvalues of $\hat{\mathbf{S}}_{\mathbf{zMn}}$ and $\hat{\mathbf{S}}_{\mathbf{zCu}}$, projection of $\hat{\mathbf{S}}_{\mathbf{Cu}}$ and $\hat{\mathbf{S}}_{\mathbf{Mn}}$ on the quantification axis. The description of the ground state of each cation cannot be directly obtained because it has to be projected on the basis formed by the eigenfunctions of $\hat{\mathbf{S}}_{\mathbf{zMn}}$ and $\hat{\mathbf{S}}_{\mathbf{zCu}}$. Using the *Clebsch-Gordan* coefficients, the ground state of the system may be written as a linear combination of two wave functions:

$$\begin{aligned}|(S_{Mn} = 5/2, S_{Cu} = 1/2), S = 2, M_S = -2> = \\ \sqrt{5/6}|S_{Mn} = 5/2, M_{SMn} = -5/2>|S_{Cu} = 1/2, M_{SCu} = 1/2> \\ -\sqrt{1/6}|S_{Mn} = 5/2, M_{SMn} = -3/2>|S_{Cu} = 1/2, M_{SCu} = -1/2>\end{aligned}$$

As these two wave functions involved in the ground state are orthogonal, the local magnetic moments carried by the Mn^{II} and the Cu^{II} cations at saturation, respectively M_{SatMn} and M_{SatCu}, can be easily obtained [2]:

$$M_{SatMn} = (5/6 * 5/2 + 1/6 * 3/2)\, g\mu_B = 4.66\,\mu_B$$
$$M_{SatCu} = (5/6 * (-1/2) + 1/6 * 1/2)\, g\mu_B = -0.66\,\mu_B$$

It is important to notice that Mn^{II} and Cu^{II} cations do not present strong magnetic anisotropy. This is why the simple model introduced earlier where $g = 2$ and where the magnetic moment has only a spin contribution is convenient for this study.

We can note here that in the case of ferromagnetic exchange interactions, this effect would not occur. The ground state arises indeed from only one wave function centred on the cations and therefore the combination of local states responsible for this magnetization loss does not take place. This effect can only be observed on systems exhibiting an antiferromagnetic exchange interaction.

The magnitude of the local magnetization loss, compared to the expected values for the free ions (5 μ_B for Mn^{II} and 1 μ_B for Cu^{II}) is not negligible since it corresponds to a loss of 7% for the Mn^{II} and 34% for the Cu^{II}. Moreover, the distribution of the *Clebsch-Gordan* coefficients depends on the value of the total spin of the system. One can show that the bigger the total spin is, the smaller the

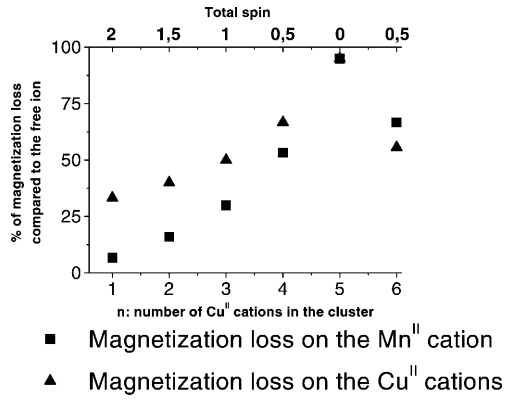

Fig. 1. Change of the magnetization loss with the number of Cu^{II} cations in the $MnCu_n$ clusters

effect is. Considering for example a molecule built with a Mn^{II} central cation, in antiferromagnetic interaction with n Cu^{II} cations. For each n value, we calculated the magnetization loss on each cation. The results are reported on Fig. 1.

The local magnetization loss is important: always above 30% for the Cu^{II} ions, it increases until $n=5$ and decreases after. The case corresponding to $n=5$ is particular with a magnetization loss of 100% on the Mn^{II} and on the Cu^{II} cations. This situation corresponds to a system where the 5 *Bohr* magnetons of the manganese ion are antiferromagnetically coupled with $5*1$ *Bohr* magnetons of the copper ions. Therefore, the resulting spin of the cluster is equal to zero and there is no more any privileged direction and any resulting local moments on the cations.

Moreover, these calculations show that the size of the cluster and more precisely the size of its spin is predominant in the magnitude of the phenomenon and this is the reason why it can be called a quantum size effect. For the infinite chain composed of numerous alternating Mn^{II} and Cu^{II} cations in an antiferromagnetic interaction, no such effect have been evidenced by PND [3].

We will show now that XMCD as PND experiments are able to evidence such an effect by choosing two compounds previously studied by PND experiments [3]. The first one is a dinuclear molecule, where the Mn^{II} cation is bridged by an oxamide ligand to one Cu^{II} cation, in an antiferromagnetic interaction ($J=-31.1\,cm^{-1}$) [5]. The second compound consists of an infinite bimetallic $(Mn^{II}Cu^{II})_n$ chain where the copper and manganese ions alternate. The bridge is an oxamate bridge and the exchange constant is $-23.4\,cm^{-1}$ [4]. The local magnetic moments carried by the Mn^{II} and Cu^{II} cations obtained by PND measurements are reported in Table 1 and compared to the calculated values obtained earlier in this work.

The values given by PND are lower than those given by the previously described calculations. That traduces the partial delocalization of the magnetic moments carriers on the ligands, expected in such compounds and not taken into account in the calculations. We will present now the XAS and XMCD results.

Determination of the Local Magnetic Moments by XMCD

X-ray Absorption Spectroscopy (XAS) is an atomic selective technique that measures the absorption cross section. During the absorption process, the atom

Table 1. Comparison of the calculated magnetic moments carried by the Mn^{II} and the Cu^{II} cations in the MnCu and $(MnCu)_n$ compounds with the experimental ones obtained by PND and by XMCD

		Calculated magnetic moments (μ_B)	Magnetic moments from PND measurements (μ_B)	Integrated area of the normalized L_3-edge signal XMCD
MnCu	Mn	4.67	4.32	$-1.07 \cdot 10^{-1}$
	Cu	−0.67	−0.47	$1.27 \cdot 10^{-2}$
	/Ratio/	6.97	*9.19*	*8.40*
$(MnCu)_n$	Mn	5	4.93	$-5.25 \cdot 10^{-2}$
	Cu	−1	−0.75	$9.31 \cdot 10^{-3}$
	/Ratio/	5	*6.57*	*5.64*

undergoes a transition from an initial state to a final state, and the cross section is expressed in the electric dipole approximation [7]. XMCD is performed when the cross section of a magnetic sample is registered for circularly polarized light [8]. When applying an external magnetic field on ferro or ferrimagnetic materials, the sample does not absorb in the same way right and left circularly polarized light, given the selection rules in the electric dipole approximation. The difference between the two absorption spectra is the XMCD signal. It is, in theory, possible to extract the quantitative value of the local magnetic moment from the XMCD signal, and to separate spin and orbital contributions, using the sum rules [9]. But it has been pointed out, for transition metal $L_{2,3}$ edges, a serious discrepancy between the magnetic moments extracted from XMCD sum rules and the expected ones [10–11]. This is often attributed to surface effect. Nevertheless, the integrated area of the XMCD signal is directly proportional to the local magnetic moment carried by the probed atom. So, this spectroscopy is well-adapted to characterize spin densities in the two materials we want to study.

We recorded the absorption and dichroic spectra at the Mn and Cu $L_{2,3}$-edges for the two compounds. At these edges, we probed selectively the 3d levels since the transitions that occur are $2p^6\ 3d^n \rightarrow 2p^5\ 3d^{n+1}$. The experimental conditions (detailed in the Experimental section) have been chosen in order to populate only the ground state and to reach the saturation of the macroscopic magnetization. XAS and XMCD spectra are reported on Fig. 2.

The XAS spectra are characteristic for Mn^{II} and Cu^{II} ions in high spin states, with numerous and well resolved structures for the Mn $L_{2,3}$-edges predicted by multiplet calculations [2, 12] and only one single peak for the copper spectrum due to the unique $3d^{10}$ electronic configuration of the final state. To be compared, the spectra presented on Fig. 2 have been normalized using the calculated spectra in the multiplet approach (not shown here). Renormalized to fully circularly polarized light for the Cu $L_{2,3}$-edges (See Experimental section), the cross sections presented here are the absolute values given by the calculations and correspond to one atom of manganese and copper.

For both compounds, whereas the Mn^{II} dichroic signal is mainly negative at low energy (L_3 edge) then positive at high energy (L_2 edge), the Cu^{II} dichroic

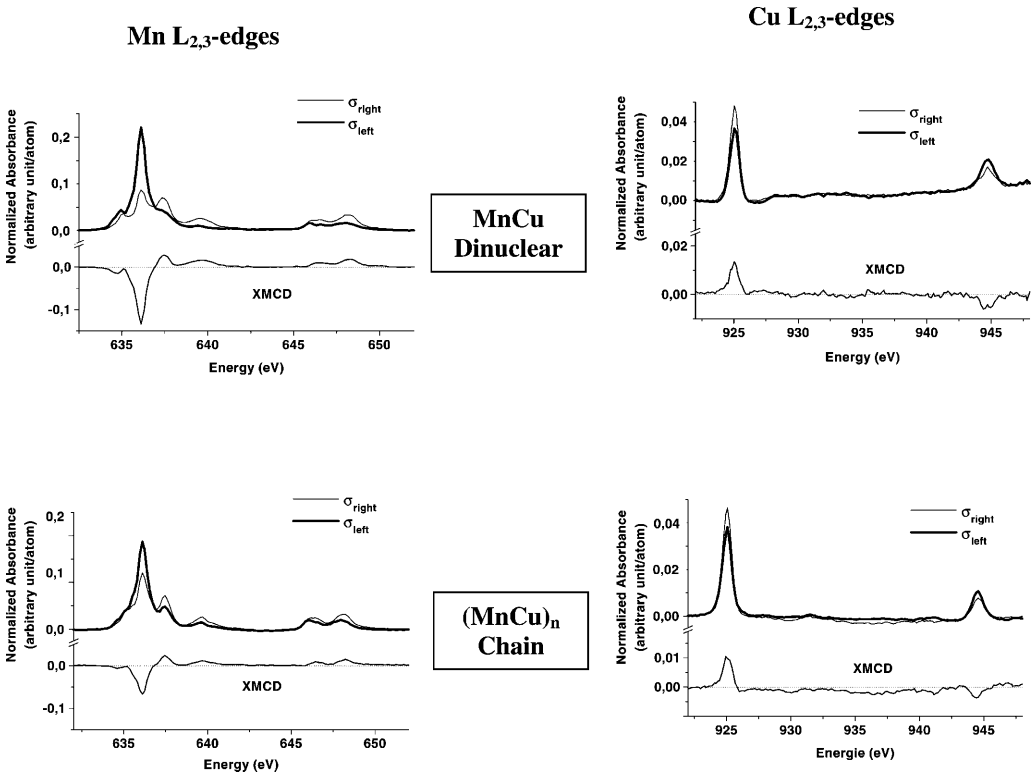

Fig. 2. Normalized XAS and XMCD spectra at the Mn and Cu $L_{2,3}$-edges for the MnCu dinuclear and the $(MnCu)_n$ chain ($T = 2\,K$, $H = \pm 5\,T$)

signal is inverse: positive at the L_3-edge and then negative at the L_2-edge. This inversion evidences directly the antiferromagnetic exchange interaction between the manganese and the copper ions, expected for these systems. Table 1 compiles the values of the integrated areas of the dichroic signals at the Mn and Cu L_3-edges for both compounds.

By considering the values reported in Table 1, one can remark that the dichroic signals at the two edges for the chain are less intense than the one of the dinuclear compound, which is surprising because we expect higher local magnetic moments. We checked experimentally that the saturation magnetization of the local magnetic moments was reached for both compounds (See Experimental section). We propose two possible origins for the low intensity of the XMCD signals obtained for the chain. Since the total electron yield detection mode is surface sensitive, one cannot discard the hypothesis that the ions at the surface of the powder grain have reduced number of magnetic neighbours or present strong magnetic anisotropy that would make the magnetization perpendicular to the surface negligible [10].

For these reasons and the difficulty to use the sum rules to extract quantitative local magnetic moments from XMCD signals, the direct comparison of PND and XMCD results is not feasible. Anyway, the comparison of the ratios of the XMCD signals integrated areas obtained at the two cations L_3-edges for each compound with the ratios of spin densities given by PND has a physical meaning. The results are reported in Table 1. The Mn/Cu ratio given by PND experiments is very

different for the two compounds, due to the magnetization loss effect observed for the dinuclear compound. For the chain as for the dinuclear compound, the results found by XMCD are in agreement with those obtained by PND: 5.64 (XMCD) compared to 6.57 (PND) for the $(MnCu)_n$ chain, 8.40 (XMCD) compared to 9.19 for the MnCu dinuclear compound.

Conclusion

This work is the first experimental evidence of magnetization loss by XMCD. These results show that XMCD experiments coupled with multiplet calculations allows to evaluate precisely magnetic moments localization in a molecule, for powdered samples for which PND cannot be used. Moreover, XMCD allows to separate spin and orbital contributions to the local magnetic moments, important for the characterization of the anisotropy, which are not given by PND. The calculations of these quantities are in progress, performing multiplet calculations with ligand field to simulate the experimental data.

After this work on reference compounds characterized by PND and XMCD, we will start XMCD experiments on new compounds of the series for which no single crystals are available. The goal is to follow by XMCD the magnetization loss of each cation in function of the molecule size, and to evaluate the spin delocalization on the ligands using this approach.

Experimental

Sample Preparation

The synthesis of the two compounds [Mn(($\pm$)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)Cu(*N*,*N*′-bis(3-aminopropyl)oxamido)] $(CF_3SO_3)_2$ ($Mn^{II}Cu^{II}$) and MnCu(1,3-propylenebis(oxamato))$(H_2O)_3 \cdot 2H_2O$ $(Mn^{II}Cu^{II})_n$ were made as described in Refs. [4] and [5].

XMCD Data Collection

The data were collected at the Beamline for Advanced diCHroism (BACH) [13] at the ELETTRA Synchrotron Radiation Source in Trieste, Italy. The radiation source was an Apple II helical undulator [14]. The first (Mn-edge) and third (Cu-edge) undulator harmonic were used, giving a circular light polarization rate equal to 100% at the Mn $L_{2,3}$ edges and 85 at the Cu $L_{2,3}$ edges. Highly monochromatic light was obtained through a variable-integrated-angle monochromator employing spherical gratings. The entrance and exit slits of the monochromator were chosen in order to set the photon energy resolution power equal to 10000 at the two edges. The sample was cooled down to 1.5 K with a $H = 5$ Tesla and 6 Tesla applied magnetic field, to check the saturation of the magnetization of the samples. Four spectra were recorded to obtain the dichroic signals, changing the circular polarization (right or left) and reversing the magnetic field applied.

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References

[1] Sessoli R, Gatteschi D, Caneschi A, Novak MA (1993) Nature **365**: 141
[2] Arrio MA, Scuillier A, Sainctavit P, Cartier dit Moulin C, Mallah T, Verdaguer M (1999) J Am Chem Soc **121**: 6414
[3] Kahn O, Mathonière C, Srinivasan B, Gillon B, Baron V, Grand A, Ohrstrom L, Ramasesha S (1997) New J Chem **21**: 1037
[4] Pei Y, Verdaguer M, Kahn O, Sletten J, Renard JP (1987) Inorg Chem **26**: 138
[5] Mathonière C, Kahn O, Daran J, Hilbig H, Kohler FH (1993) Inorg Chem **32**: 4057
[6] Baron V, Gillon B, Plantevin O, Cousson A, Mathonière C, Kahn O, Grand A, Ohrstrom L, Delley B (1996) J Am Chem Soc **118**: 11822
[7] Koningsberger DC, Prins R (eds) (1987) X-ray absorption: principles, applications, techniques of EXAFS, SEXAFS and XANES vol 92, Wiley, New York
[8] Beaurepaire E, Scheurer F, Krill G, Kappler JP (eds) (2001) Magnetism and synchrotron radiation. Springer, Berlin
[9] Thole BT, Carra P, Sette F, van der Laan G (1992) Phys Rev Lett **68**: 1943
[10] Arrio MA, Sainctavit P, Cartier dit Moulin C, Brouder C, de Groot FMF, Mallah T, Verdaguer M (1996) J Phys Chem **100**: 4679
[11] Sainctavit P, Cartier dit Moulin C, Arrio M-A (2001) Magnetic Measurements at the Atomic Scale in Molecular Magnetic and Paramagnetic Compounds. In: Magnetism: Molecules to Materials, Miller JS, Drillon M (eds), Wiley VCH Verlag, Berlin, p 131
[12] Arrio MA, Sainctavit P, Cartier dit Moulin C, Mallah T, Verdaguer M, Pellegrin E, Chen CT (1996) J Am Chem Soc **118**: 6422
[13] Zangrando M, Finazzi M, Paolucci G, Comelli G, Diviacco B, Walker RP, Cocco D, Parmigiani F (2001) Rev Sci Instrum **72**: 1313
[14] Sasaki S (1994) Nucl Instrum Methods Phys Res A **347**: 83