Strong Hard X-ray Magnetochiral Dichroism in Paramagnetic Enantiopure Molecules

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The synergy between different physical properties in a single material may give rise to the appearance of unprecedented new physical phenomena. Molecule-based materials are particularly suitable for the development of multifunctionality, since different building blocks can be combined in a bottom-up approach to deliver tailor-made molecular materials with two or more properties of interest. Many molecule-based materials with combination of electrical, magnetic, and/or optical properties have been successfully studied with this purpose.[1–8] In the case of new phenomena from magneto-optical interactions, one of the most unprecedented effects is the so-called magnetochiral dichroism (MChD).[9,10] It is a physical phenomenon expected to emerge in optically active magnetic media arising from the synergy between magnetism and chirality. Symmetry arguments indicate that optical properties of chiral systems should be anisotropic with respect to the relative orientation between light and an applied magnetic field. In other words, the light–matter interaction should show different quantum yields if light propagates parallel or antiparallel to the magnetic field direction,[11] and this should occur for unpolarized light. The first experimental evidence of this second-order effect was reported in 1997 by Rikken.[12] In his seminal work, he was able to detect the anisotropy of the luminescence intensity in a chiral europium(III) complex when it is excited in solution with UV light. MChD seems to lie in the chiral nature of the chemical structure as demonstrated in simple and elegant theoretical approaches for free electrons in infinite helixes.[13] A semiclassical approach based on a dipole interaction model indicated that even organic molecules may exhibit this phenomena.[14]

Since its experimental discovery in luminiscence, MChD has been reported for absorption,[15,16] photochemistry,[17] Bragg scattering,[18] and refraction.[19] In all these cases, the effect is observed in the visible light region and it is very weak, but measurable (less than 0.01% of the corresponding signal). Although a detailed quantum mechanical molecular theory was developed to describe and predict this phenomenon,[9] it is difficult to translate this knowledge into the chemical design of molecular materials in the search for strong MChD. The experimental data suggest some important factors to be taken into account. It was demonstrated that the appearance of magnetic ordering enhances the effect about one order of magnitude.[20] The fact that the same center is at the origin of chirality and magnetism is most probably a crucial point for the appearance of a magnetochiral dichroic effect.[21] It was rationalized that the largest MChD effects should be found in the absorption bands of certain lanthanide complexes.[9] However, in most lanthanide and/or metal complexes, the active electronic transitions in the visible region are forbidden by dipolar selection rules, being essentially weak.

We decided to investigate the existence of MChD in hard X-ray absorption spectroscopy (XAS). XAS seemed a good candidate for the observation of this second-order effect. It shows much higher extinction coefficients and penetration depths than typical UV-vis experiments, allowing to obtain better signal-to-noise ratio for the putative MChD. Actually, X-ray MChD (XMChD) was used as a probe for the detection of the time-reversal odd part in magnetoelectric materials.[22] However, the authors reported the observation of Cr-K edge XMChD in either oriented Cr_2O_3 antiferromagnetic single crystals or in single domain antiferromagnetic Cr_2O_3 powder samples at 50 K. In these cases, XMChD is induced by the anisotropic magnetic ordering but not from the intrinsic interplay between magnetic centers and chirality in a molecule without magnetic ordering.

The presence of MChD in the X-ray region was already suggested by Barron.[23] In contrast with the related natural X-ray circular dichroism,[24] where oriented samples are needed, XMChD should be observed in isotropic samples because of the electric dipole-electric quadrupole mechanism that originates X-ray dichroic phenomena. Experimentally, the measurement of XMChD presents several technical problems. XMChD studies would be ideally performed with unpolarized light but, obviously, synchrotron radiation was needed. We used a MCD beam line, originally optimized for experiments with circularly polarized light. We centered the sample vertically on the plane of the electron orbit of the storage ring in order to avoid any contaminant circular polarization. Still, the linear polarization of the beam could not be avoided. We minimized possible artifacts by applying the magnetic field perpendicular to the polarization plane. In such unideal conditions, we rationalized that only a molecular material with strong MChD would give a detectable effect.

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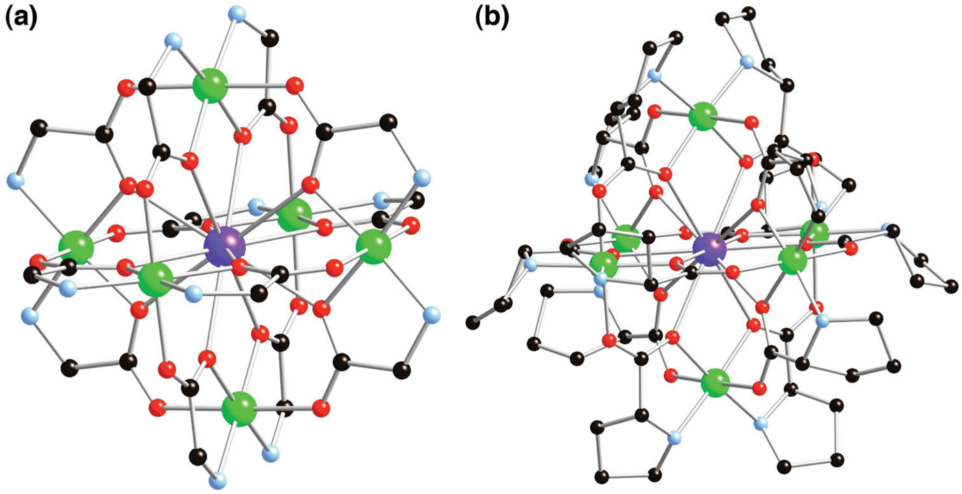

Figure 1. Representation of the molecular structure of the $\{Tb[Ni(L\text{-}pro)_2]_6\}^{3+}$ cluster (a) and detail of the high-symmetry core, where the ring carbon atoms in the prolinate ligands have been omitted for clarity (b). Atom scheme: Tb, purple; Ni, green; O, red; C, black; N, blue.

As materials, we prepared the chiral cations of formula $\{Tb[Ni(pro)_2]_6\}^{3+}$ (pro = L,D-prolinate). These clusters are isostructural to those reported for other rare earths (RE), such as Sm or Gd.[25,26] The RE^{3+} cation occupies the center of an icosahedra, surrounded by six $Ni(pro)_2$ units. The Ni^{2+} centers form a perfect octahedra (**Figure 1**), and the pro ligands occupy the equatorial positions of the Ni^{2+} octahedral coordination. The RE^{3+} center is coordinated by twelve oxygen atoms directly bound to the Ni^{2+} ions. The other oxygen atom in the carboxylate group coordinates the axial positions of an adjacent Ni^{2+} ion. This carboxylate multibridged structure creates a very stable molecular cation also in solution. These cationic clusters crystallize in the *F*23 space group. The packing is always controlled by the cations, with anions and solvent occupying the holes in a highly symmetric structure. Indeed, the same unit cell has been found for a variety of inorganic anions or a mixture of them and even when these clusters form mixed crystals with additional simple salts.[27] These cations are paramagnetic, with weak intramolecular magnetic superexchange. We incorporated Tb^{3+} as the RE center because of its larger magnetic anisotropy. These derivatives appear to be ideal systems to study hard X-ray MChD (XMChD) in absorption spectroscopy for several reasons: i) lanthanides are expected to give the larger MChD, as theoretically and experimentally confirmed; ii) lanthanide ions have particularly high X-ray absorption coefficients, which could give rise to strong absorption and thus statistically significant XMChD; iii) among the lanthanides, Tb complexes usually posses high magnetic anisotropy, which has already yielded unusual magnetic properties;[28] iv) the presence of two different metal centers allows for a multi-metal study, to gather MChD data from a same material at different absorption centers; v) the two different enantiopure molecules, with L- or D-prolinate, are easily prepared, and chirality is maintained through the whole process (no racemization).

The enantiomers $\{Tb[Ni(L\text{-}pro)_2]_6\}^{3+}$ and $\{Tb[Ni(D\text{-}pro)_2]_6\}^{3+}$ were prepared as mixed nitrate/perchlorate salts to obtain pure high-quality single crystals.[27] The single crystals were hand-collected and their purity was confirmed by elemental analysis, X-ray diffraction, UV-vis spectroscopy, and mass spectrometry (see the SI). The enantiopurity was confirmed by circular dichroism (see Figure 2 and 3 of the SI). Single crystals were ground into a fine powder for the XAS experiments, to obtain isotropic samples. We gathered data on the L_2 (8252 eV) and L_3 (7514 eV) Tb absorption edges, with an applied magnetic field (B = 1 T) either parallel or anti-parallel to the direction of beam propagation. The onset of the absorption spectrum determined from the maximum of the first derivative of the XANES (X-ray Absorption Near Edge Structure) data were systematically up shifted ~7 eV (L_3) and ~10 eV (L_2) above the value quoted for metallic Tb indicating that Tb absorbers were in an oxidized form, most probably +3 oxidation state (**Figure 2**). The

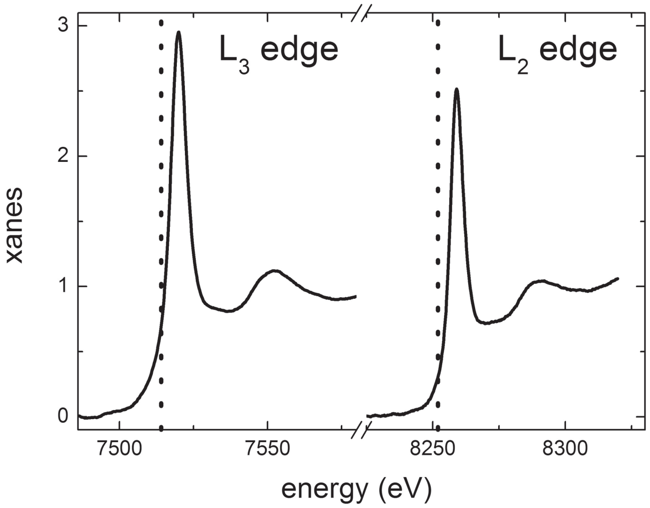

Figure 2. XANES spectra obtained for $\{Tb[Ni(L\text{-}pro)_2]_6\}^{3+}$ at Tb L_2 (right) and L_3 (left) absorption edges. Dashed vertical lines indicate the position of the absorption edges expected for zero-valent Terbium. The XANES spectra for the D-form of the cluster were identical to the one obtained for the L-form.

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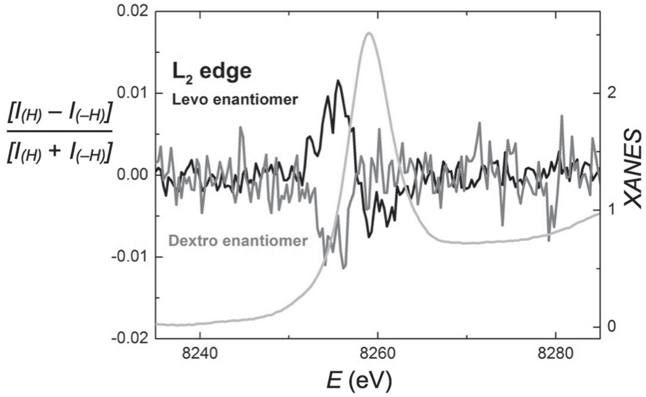

Figure 3. Dichroism signals obtained from XANES experiment at Tb L_2 from both, $\{Tb[Ni(L\text{-}pro)_2]_6\}^{3+}$ (black) and $\{Tb[Ni(D\text{-}pro)_2]_6\}^{3+}$ (grey) enantiomers. The light grey curve is the corresponding XANES spectra superimposed on the dichroism signals. Dichroism: difference between normalized XAS spectra obtained with the magnetic field parallel and anti-parallel to the photon beam.

field-averaged XANES spectra obtained from the L and D enantiomers were identical within experimental errors as expected.

Figure 3 displays the dichroic spectra obtained at the L_2 edge of terbium: the difference between normalized XAS spectra obtained with the magnetic field parallel and anti-parallel to the photon beam. We indeed observe an effect of the magnetic field on the X-ray absorption depending on the energy of the radiation, and a sign inversion when changing the helicity of the molecule from L to D. XMChD appears as the exact mirror image when comparing the data for each enantiomer, as in typical dichroic phenomena. XMChD reaches a maximum of 1% of the total intensity about the Tb L_2 edge. This is relatively the largest MChD effect observed, including even magnetically ordered or structurally oriented samples. This hints that strong XMChD (and probably MChD at other regions of the electromagnetic spectrum) is essentially originated by the local spin–orbit coupling, and not from collective events. Therefore, the enhancement of MChD in a magnetically ordered phased should probably be related to the appearance of an additional internal magnetic field.

Surprisingly, we were not able to detect a net dichroic effect in the Tb L_3 edge, that could be unambigously assigned to the appearance of XMChD beyond the experimental error. The $L_{2,3}$ edges have well-defined and different initial states, $2p_{1/2}$ core state for the L_2 edge and the $2p_{3/2}$ core state for the L_3 edge. The final states are the 5d for the electric dipole and the 4f for the electric quadrupole. It has been predicted theoretically that the Tb L_2 edge should give rise to stronger dichroic phenomena.[29,30] We neither observed any significant XMChD at the Nickel K-edge. This result, on the contrary, was expected since transition metals have much weaker spin–orbit coupling, weaker absorbance, and weaker contribution of the electric quadrupole that should have an important influence in the appearance of dichroism.

In conclusion, we have discovered for the first time the existence of core X-ray absorption magnetochiral dichroism in paramagnetic enantiopure molecules. The mixed rare-earth/transition-metal complexes were rationally designed to observe the phenomenon, comprising different metal centers and easy-to-prepare enantiopure building blocks. We have found XMChD intensities up to 1% in the Tb L_2 absorption edge at room temperature, at relatively low magnetic fields (1 T), and with isotropic samples. These values are larger than those observed for visible-light experiments, and also in the X-ray absorption of oriented magnets at very low temperatures. Our results support the theoretical predictions and bring some important conclusions that may help to design new materials with enhanced XMChD. Direct participation of unpaired electrons is not necessary for the appearance of MChD, since in our XAS experiments we are exciting non-magnetic core electrons in a paramagnetic sample without magnetic ordering. Even highly symmetric molecules, icosahedral in this case, can still give rise to strong dichroism if chiral. And the electronic origin must be essentially related to the spin–orbit coupling (anisotropy) of the local electrons. It will be of great interest to study the XMChD of the isostructural $\{RE[Ni(pro)_2]_6\}^{3+}$ family for all rare earth cations to determine the influence of magnetic anisotropy in MChD. These experiments are in progress.

Beyond these basic considerations, our findings suggest that a much stronger XMChD could appear. We used a fixed 1 T magnet, whereas measurements at different magnetic fields should show a linear field dependence. Experiments with oriented single crystals should yield stronger XMChD since the relative orientation between the magnetic field and molecular polarization axis could be controlled and optimized. Finally, in analogous materials able to exhibit magnetic ordering, XMChD should also increase about an order of magnitude as in past MChD experiments. This suggests that XMChD accounting for over 10% of the total absorption might be achieved.

Experimental Section

Synthesis: All reagents were commercially available (>99.9%, Sigma-Aldrich) and were used without further purification. $[Ni(pro)_2]$ and the $\{Tb[Ni(pro)_2]_6\}^{3+}$ salts were prepared from optimized literature methods.[27,31]

X-ray Absorption Spectroscopy: X-ray Absorption Spectroscopy (XAS) experiments were performed using the D06A-DXAS beam line of Laboratorio Nacional de Luz Sincrotron (LNLS), Campinas, Brazil. The sample was vertically centered on the plane of the electron orbit of the storage ring in order to eliminate circularly polarized light. Sample temperature was set to 22 ± 1 °C. The magnetic field applied to the sample was obtained from a rotator permanent magnet with an effective field at sample position B = 1 T. The incoming X-ray beam was focalized on the sample holder using a curved Si(111). Individual XAS spectra were obtained using a liquid-nitrogen-cooled CCD camera. Sequences of XAS spectra with different relative orientations (either parallel (+) or anti-parallel (−)) between the applied magnetic field and the direction of propagation of the X-ray beam were used to construct both, the XANES and the XMChD spectra. The acquisition sequence (+−−+−++−) was designed to avoid hysteresis due to field inversion, and suitable waiting time (1 second) between spectra was allowed to ensure the reproducibility of the field strength at sample position. XANES spectra were obtained as the simple arithmetic average of the collected spectra and XMChD was obtained as the difference in between.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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[1] J. S. Miller, *Chem. Soc. Rev.* **2011**, *40*, 3266.
[2] J. R. Galan-Mascaros, E. Coronado, P. A. Goddard, J. Singleton, A. I. Coldea, J. D. Wallis, S. J. Coles, A. Alberola, *J. Am. Chem. Soc.* **2010**, *132*, 9271.
[3] J. Milon, M.-C. Daniel, A. Kaiba, P. Guionneau, S. Brandes, J.-P. Sutter, *J. Am. Chem. Soc.* **2007**, *129*, 13872.
[4] J. Letard, P. Guionneau, O. Nguyen, J. Costa, S. Marcen, G. Chastanet, M. Marchivie, L. Goux-Capes, *J. Am. Chem. Soc.* **2005**, *11*, 4582.
[5] C. Mathoniere, R. Podgajny, P. Guionneau, C. Labrugere, B. Sieklucka, *Chem. Mater* **2005**, *17*, 442.
[6] J. Herrera, V. Marvaud, M. Verdaguer, J. Marrot, M. Kalisz, C. Mathoniere, *Angew. Chem. Int. Ed.* **2004**, *43*, 5468.
[7] O. Sato, Y. Einaga, A. Fujishima, K. Hashimoto, *Inorg. Chem.* **1999**, *38*, 4405.
[8] S.-W. Cheong, M. Mostovoy, *Nature Mater* **2007**, *6*, 13.
[9] L. D. Barron, J. Vrbancich, *Mol. Phys.* **1984**, *51*, 715.
[10] L. D. Barron, *Nature Mater.* **2008**, *7*, 691.
[11] N. B. Baranova, B. Y. Zeldovich, *Mol. Phys.* **1979**, *38*, 1085.
[12] G. L. J. A. Rikken, E. Raupach, *Nature* **1997**, *390*, 493.
[13] G. H. Wagniere, G. L. J. A. Rikken, *Chem. Phys. Lett.* **2009**, *481*, 166.
[14] T. Rouchon, M. Vallet, D. Chauvat, A. LeFloch, *J. Chem. Phys.* **2006**, *125*, 084104.
[15] G. L. J. A. Rikken, E. Raupach, *Phys. Rev. E* **1998**, *58*, 5081.
[16] Y. Kitagawa, H. Segawa, K. Ishii, *Angew. Chem. Int. Ed.* **1984**, *51*, 715.
[17] G. L. J. A. Rikken, E. Raupach, *Nature* **2000**, *405*, 932.
[18] C. Koerdst, G. Duchs, G. L. J. A. Rikken, *Phys. Rev. Lett.* **2003**, *91*, 073902.
[19] P. Kleindienst, G. H. Wagniere, *Chem. Phys. Lett.* **1998**, *288*, 89.
[20] C. Train, R. Gheorghe, V. Krstic, L. M. Chamoreau, N. S. Ovanesyan, G. L. J. A. Rikken, M. Gruselle, M. Verdaguer, *Nature Mater.* **2008**, *7*, 729.
[21] F. Pointillart, M. Gruselle, G. Andre, C. Train, *J Phys. Cond. Matter.* **2008**, *20*, 135214.
[22] J. Goulon, A. Rogalev, F. Wilhelm, C. Goulon-Ginet, P. Carra, D. Cabaret, C. Brouder, *Phys. Rev. Lett.* **2002**, *88*, 237401.
[23] L. D. Barron, *Molecular Light Scattering and optical activity*, 2nd Ed. Cambridge University Press, **2004**.
[24] R. D. Peacock, B. Stewart, *J. Phys. Chem. B* **2001**, *105*, 351.
[25] Y. Yukawa, S. Igarashi, A. Yamano, S. Sato, *Chem. Commun.* **1997**, 711.
[26] Y. Yukawa, G. Aromi, S. Igarashi, J. Ribas, S. A. Zvyagin, J. Krzystek, *Angew. Chem. Int. Ed.* **2005**, *44*, 1997.
[27] S. Igarashi, Y. Hoshino, Y. Masuda, Y. Yukawa, *Inorg. Chem.* **2000**, *39*, 2509.
[28] N. Ishikawa, M. Sugita, W. Wernsdorfer, *Angew. Chem. Int. Ed.* **2005**, *44*, 2931.
[29] K. Fukui, H. Ogasawara, A. Kotani, *Phys. Rev. B* **2001**, *64*, 104405.
[30] M. Nakazaawa, K. Fukui, A. Kotani, *J. Solid State Chem.* **2003**, *171*, 295.
[31] T. Yasui, J. Hidaka, Y. Shimura, *J. Chem. Soc.* **1965**, *87*, 2762.

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