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► **To cite this version:**

Matteo Atzori, Miguel Cortijo, Elisabeth A. Hillard, Rikken G.L.J.A., Andrei Rogalev, et al.. Chirality determination in single crystals using XNCD and MChD. 33rd European Crystallography Meeting, ECM, Aug 2022, Versailles, France. pp.e718-e718, 10.1107/S2053273322090611 . hal-04293311

HAL Id: hal-04293311

<https://hal.science/hal-04293311v1>

Submitted on 20 Nov 2023

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MS31-1-1 Chirality determination in single crystals using XNCD and MChD

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Abstract

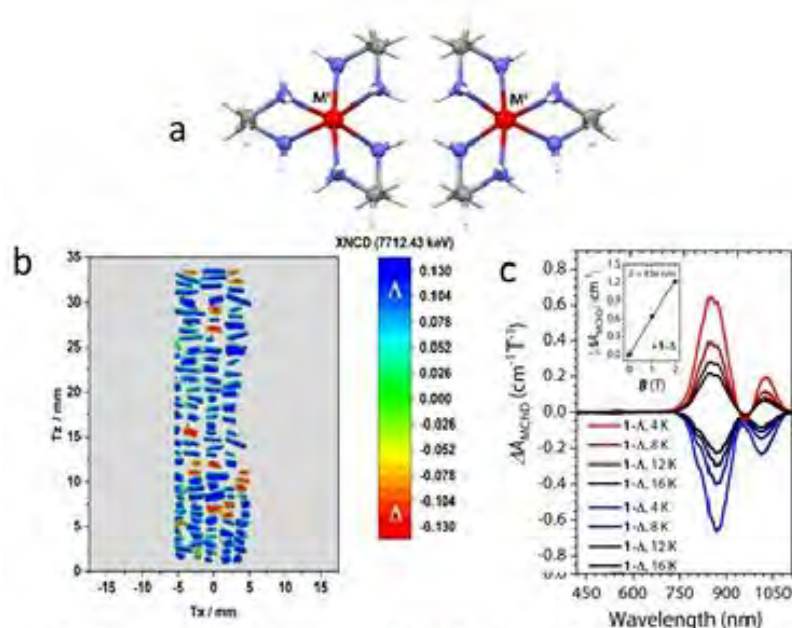
Octahedral tris(bidentate) coordination complexes are chiral due to the propeller-like arrangement of the ligands around the metal core. The enantiomers of $[M(en)_3](NO_3)_2$ ($M = Mn(II), Co(II), Ni(II), Zn(II)$; en = ethylenediamine) spontaneously resolve to form a mixture of conglomerate crystals in the space group $P6_322$ at room temperature [1].

Although conglomerate formation allows crystals of only one or the other enantiomer to be effortlessly obtained, resolution can only truly be accomplished after the identification and triage of the two crystal forms. For this, we have implemented an original method for determining the handedness of individual crystals in a mixture using a tightly-focused, circularly polarized X-ray beam [2]. The X-ray natural circular dichroism (XNCD) spectra measured at the metal K-edge on $[Co(en)_3](NO_3)_2$ and $[Ni(en)_3](NO_3)_2$ show maxima at the metal pre-edge. Mapping of a crystal assembly was performed by setting the X-ray energy to the peak maximum and determining the sign of the difference in absorption for the two polarizations, directly yielding the crystal handedness. Interestingly, small amounts of ascorbic acid present in the crystallization flask appear to bias the conglomerate, in the lambda direction for $[Co(en)_3](NO_3)_2$ and in the delta direction for $[Ni(en)_3](NO_3)_2$.

Using the same model compounds, we have obtained experimental magneto-chiral dichroism (MChD) spectra on single crystals in the UV-visible energy range. MChD manifests as the differential absorption of chiral systems under a magnetic field using unpolarized light. The paramagnetic nickel and cobalt derivatives demonstrate an enormous optical anisotropy with MChD on the order of 10^{-1} with respect to the isotropic absorption spectra [3]. State-of-the-art quantum chemical calculations of the MChD spectra for the Ni(II) derivative were able to simulate the experimental results. This opens the way to new tools to assign chirality using unpolarized light and the development of MChD as a potent spectroscopic tool.

References

- (1) Cortijo, M.; Valentín-Pérez, Á.; Rouzières, M.; Clérac, R.; Rosa, P.; Hillard, E. A. *Crystals* 2020, 10 (6), 472.
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- (3) M. Atzori, H.D. Ludowieg, Á. Valentín-Pérez, M. Cortijo, I. Breslavetz, K. Paillot, P. Rosa, C. Train, J. Autschbach, E.A. Hillard, G.L.J.A. Rikken, *Sci. Adv.*, 7 (2021) eabg2859.



(a) View of the molecular structure of Λ - $[M^{II}(en)_3]^{2+}$ (left) and Δ - $[M^{II}(en)_3]^{2+}$ (right) ($M^{II} = Ni, Co$) complex cations; (b) XNCD mapping of an assembly of $[Co^{II}(en)_3](NO_3)_2$ crystals; (c) Orthoaxial ΔA_{MChD} spectra for Λ and Δ single crystals of $[Ni^{II}(en)_3](NO_3)_2$ at several temperatures. The inset shows the MChA strength as a function of the inverse temperature.