

X-ray optical activity of a tricobalt metal atom chain

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A simple procedure based on anion exchange was employed for the enantiomeric resolution of the extended metal atom chain (EMAC) $[\text{Co}_3(\text{dpa})_4(\text{MeCN})_2]^{2+}$. Use of the chiral anion $[\text{As}_2(\text{tartrate})_2](\text{NBu}_4)_2$, (Λ -1 or Δ -1), resulted in the selective crystallization of the EMAC enantiomers as diastereomeric $[\Delta\text{-Co}_3(\text{dpa})_4(\text{MeCN})_2][\text{NBu}_4]_2[\Lambda\text{-As}_2(\text{tartrate})_2]_2$, (Δ -2) and $[\Lambda\text{-Co}_3(\text{dpa})_4(\text{MeCN})_2][\text{NBu}_4]_2[\Delta\text{-As}_2(\text{tartrate})_2]_2$ (Λ -2), respectively, in the $P4_212$ space group, whereas a racemic mixture of **1** yielded $[\text{Co}_3(\text{dpa})_4(\text{MeCN})_2][\text{As}_2(\text{tartrate})_2]\cdot 2\text{MeCN}$ (*rac*-3), which crystallized in the $C2/c$ space group. The local electronic and magnetic structure of the EMAC enantiomers was studied, exploiting a variety of dichroisms in single crystals [1]. A strong linear dichroism at the Co K-edge was observed in the orthoaxial configuration, whereas it vanished in the axial orientation, thus spectroscopically confirming the D_4 crystal symmetry. Compounds Δ -2 and Λ -2 are shown to be enantiopure materials as evidenced by mirror-image natural circular dichroism spectra in the UV/vis in solution and in the X-ray range at the Co K-edge in single crystals (Fig.1). The surprising absence of detectable X-ray magnetic circular dichroism or X-ray magnetochiral dichroism signals at the Co K-edge, even at low temperature (3 K) and a high magnetic field (17 Tesla), is ascribed to a strongly delocalized spin density on the cobalt ions [2].

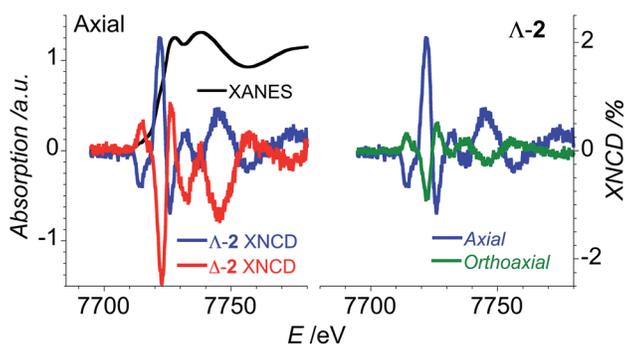


Fig.1: (a) XANES and XNCD spectra in axial configuration (Theta=0) for Delta-2 (red) and Lambda-2 (blue); (b) comparison of axial (blue) and orthoaxial (green) XNCD spectra for Lambda-2

[1] J. Goulon, A. Rogalev, F. Wilhelm, C. Goulon-Ginet, P. Carra, I. Marri, Ch. Brouder. "X-ray optical activity: applications of sum rules". *ZhETF (JETP)*, 2003, vol. 124, p.445

[2] Anandi Srinivasan, Miguel Cortijo, Vladimir Bulicanu, Ahmad Naim, Rodolphe Clérac, Philippe Saintavit, Andrei Rogalev, Fabrice Wilhelm, Patrick Rosa, Elizabeth A. Hillard*. "Enantiomeric resolution and X-ray optical activity of a tricobalt extended metal atom chain". *Chemical Science*, 2018 (first published on 4 December 2017)

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