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Tris(ethylenediamine) cobalt(II) and manganese(II) nitrates: synthesis, structure and crystal handedness mapping by X-ray circular dichroism

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Abstract: Enantiomers of $[Ni(en)_3](NO_3)_2$ and $[Zn(en)_3](NO_3)_2$ (en = ethylenediamine) spontaneously resolve to form a conglomerate, and present a reversible phase transition from space group $P6_322$ to $P6_522$ or $P6_122$. To extend the family of such compounds, we have investigated the isostructural $[Mn(en)_3](NO_3)_2$ and $[Co(en)_3](NO_3)_2$. The Mn(II) analogue undergoes the same phase transition at 150(2) K, while the Co(II) derivative does not demonstrate a phase transition down to 2 K.[1]
Although conglomerate formation allows non-centrosymmetric crystals to be effortlessly obtained, spontaneous resolution is only accomplished after the identification crystal handedness. 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 spectra measured at the metal K-edge on crystals of $[Co(en)_3](NO_3)_2$ and $[Ni(en)_3](NO_3)_2$ show maxima at the metal pre-edge. A mapping of a collection of crystals was performed at this energy; the sign of the difference in absorption for the two polarizations directly yields the handedness of the crystal.

1) M. Cortijo, A. Valentin-Perez, M. Rouzières, R. Clérac, P. Rosa, E.A. Hillard, *Crystals*, 2020, 10(6), 472 https://doi.org/10.3390/cryst10060472.

2) M. Cortijo, A. Valentin-Perez, A. Rogalev, F. Wilhelm, Ph. Sainctavit, P. Rosa, E.A. Hillard, *Chem. Eur. J.*, 2020, https://doi.org/10.1002/chem.202001783

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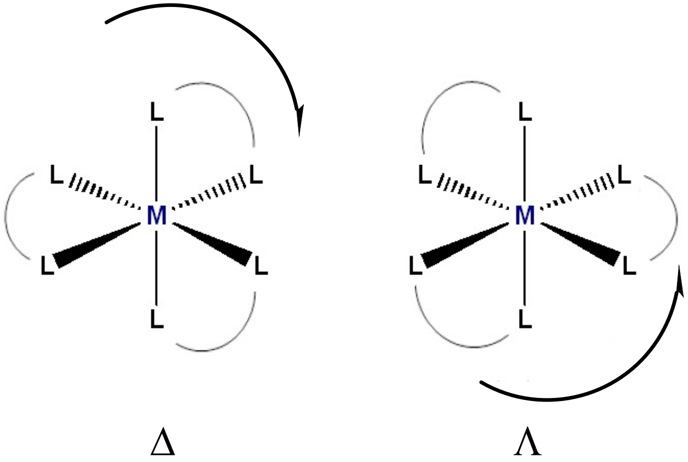
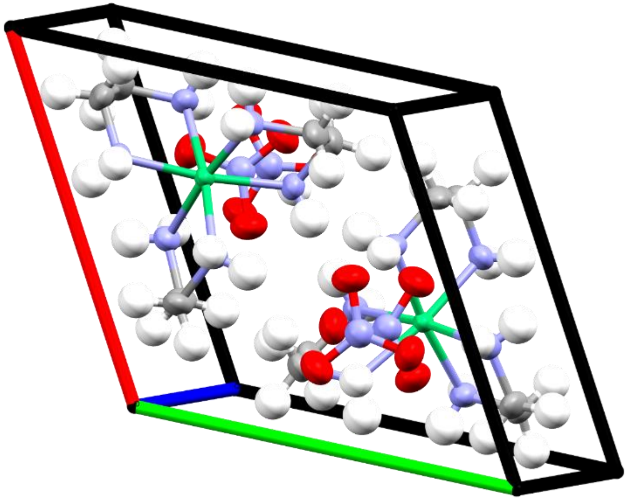
Introduction

Chirality in octahedral coordination compounds



Octahedral tris(bidentate) coordination complexes demonstrate helicoidal chirality due to the clockwise or counter-clockwise arrangement of the ligands around the metal core.



Δ-$[Ni(en)_3](NO_3)_2$ in the $P6_322$ phase

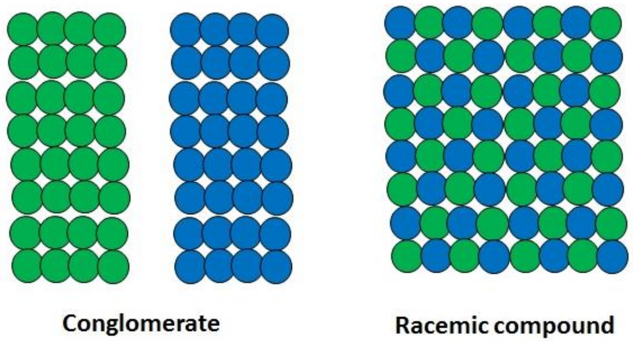
An example is $[Ni(en)_3](NO_3)_2$ (*en* = *ethylenediamine*) which crystallizes in the space group $P6_322$ at room temperature.

L. J. Farrugia et al. *J. Appl. Cryst.* **2003**, *36*, 141.

Introduction

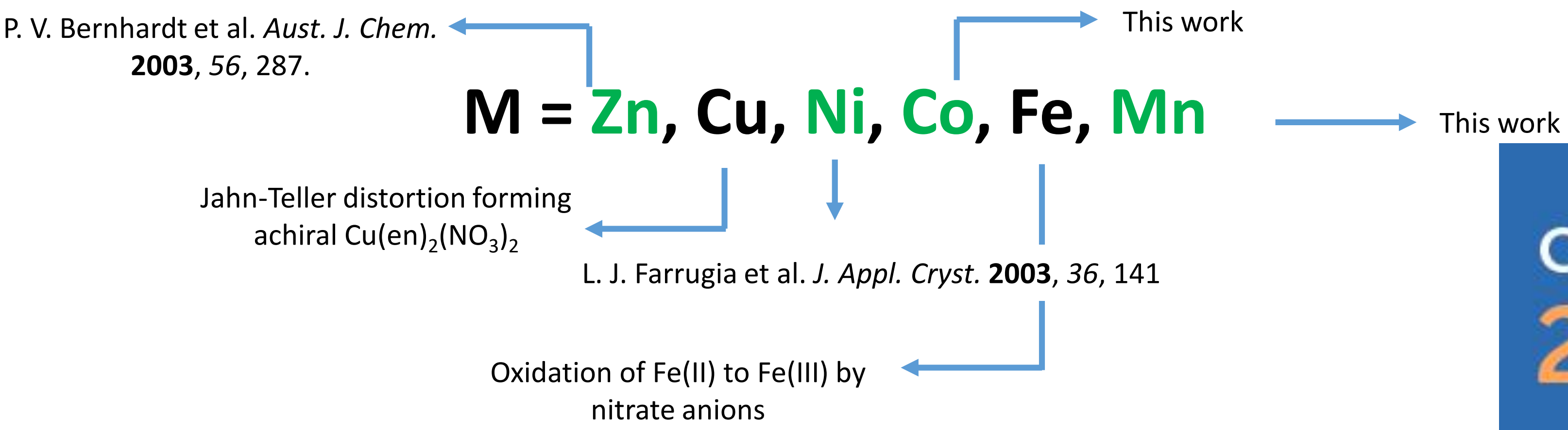
$[M(en)_3](NO_3)_2$: Noncentrosymmetric crystals

As part of our interest in X-ray natural circular dichroism (XNCD), we wished to extend this series of $[M(en)_3](NO_3)_2$ compounds to obtain non-centrosymmetrc crystals of optical quality and high crystal symmetry.



The known Ni(II) and Zn(II) complexes undergo spontaneous resolution by conglomerate formation, such that the enantiomers segregate into non-centrosymmetric crystals.

Attempts were made to synthesize complexes of the late transition metals, and the new Mn(II) and Co(II) analogues were obtained.



P. V. Bernhardt et al. *Aust. J. Chem.* **2003**, *56*, 287.

This work

M = Zn, Cu, Ni, Co, Fe, Mn

This work

Jahn-Teller distortion forming achiral $Cu(en)_2(NO_3)_2$

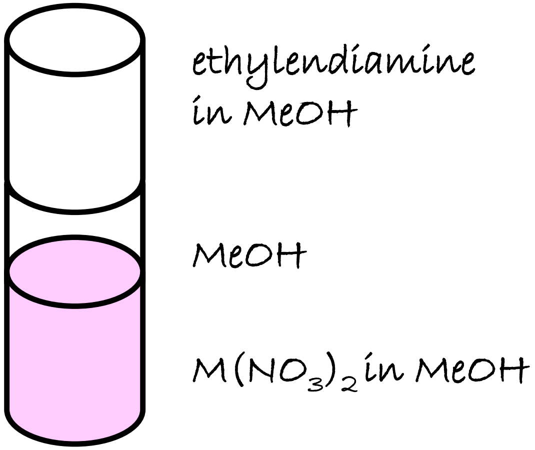
L. J. Farrugia et al. *J. Appl. Cryst.* **2003**, *36*, 141

Oxidation of Fe(II) to Fe(III) by nitrate anions

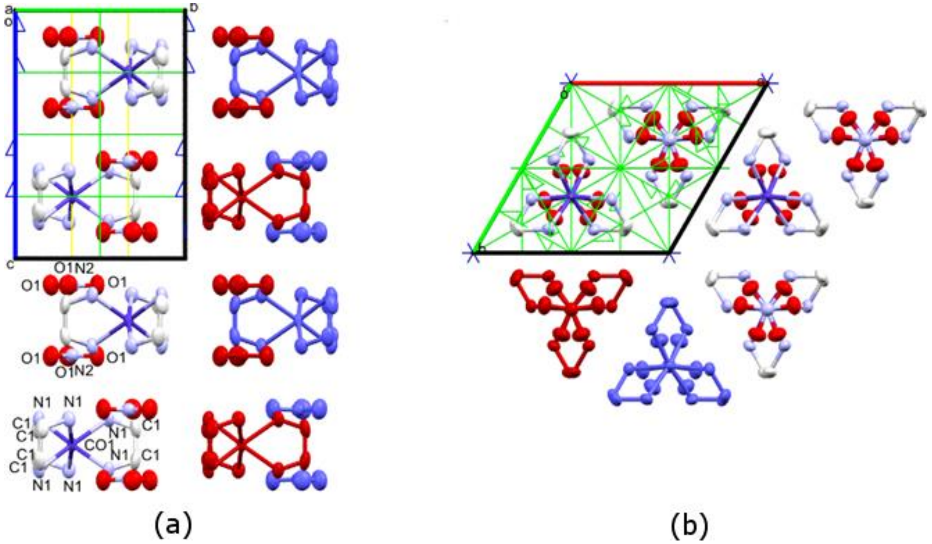
Results and discussion

Manganese(II) and cobalt(II) derivatives

$[Mn(en)_3](NO_3)_2$ and $[Co(en)_3](NO_3)_2$ were found to be isostructural to the Zn(II) and Ni(II) derivatives, crystallizing as conglomerates in $P6_322$ at room temperature.



Crystallization of $[Mn(en)_3](NO_3)_2$ and $[Co(en)_3](NO_3)_2$ via slow diffusion of methanolic solutions in inert atmosphere. L-ascorbic acid was added as an antioxidant to the Co(II) reaction.



Anisotropic displacement ellipsoid plot (Mercury, 50% probability) of Δ-$[Co(en)_3](NO_3)_2$ at 298 K as viewed down the (a) *a* and (b) *c* crystal axes. Space group $P6_322$. Unit cell and symmetry axes are shown, with blue = 6-fold screw, yellow = 3-fold and green = 2-fold axes. Different columns are indicated by red and blue molecules. H atoms omitted for clarity.

M. Cortijo, A. Valentin-Perez, M. Rouzières, R. Clérac, P. Rosa, E.A. Hillard, *Crystals*, 2020, 10(6), 472 https://doi.org/10.3390/cryst10060472.

Results and discussion

Crystallographic data for $[M(en)_3](NO_3)_2$ at 298 K

	Δ-Mn	Λ-Mn	Δ-Co	Λ-Co
Formula	$C_6H_{24}MnN_8O_6$	$C_6H_{24}MnN_8O_6$	$C_6H_{24}CoN_8O_6$	$C_6H_{24}CoN_8O_6$
Formula weight	359.25	359.25	363.26	363.26
Crystal system	hexagonal			
Space group	$P6_322$ (no. 182)			
a, *b*	9.057(3) Å	9.0572(7) Å	8.9285(8) Å	8.9158(8) Å
c	11.301(3) Å	11.3115(10) Å	11.3126(11) Å	11.2970(10) Å
α, *β*	90°			
γ	120°			
Volume	802.8(4) Å³	803.60(11) Å³	781.00(16) Å³	777.70(16) Å³
Z	2			
ρ_{calc}	1.4861 g/cm³	1.4846 g/cm³	1.545 g/cm³	1.551 g/cm³
μ (Mo Kα)	0.861 mm⁻¹	0.860 mm⁻¹	1.138 mm⁻¹	1.143 mm⁻¹
Reflections collected	21940 (5.2° ≤ 2θ ≤ 56.6°)	9221 (5.2° ≤ 2θ ≤ 52.8°)	6378 (5.3° ≤ 2θ ≤ 52.7°)	20782 (6.4° ≤ 2θ ≤ 52.9°)
Unique	675 [R_{int} = 0.0356]	560 [R_{int} = 0.0301]	545 [R_{int} = 0.0216]	542 [R_{int} = 0.0213]
Final *R* indexes [all data]	R_1 = 0.0279 wR_2 = 0.0742	R_1 = 0.0343 wR_2 = 0.0894	R_1 = 0.0232 wR_2 = 0.0766	R_1 = 0.0176 wR_2 = 0.0462
Flack para.	0.07(5)	0.04(7)	-0.007(8)	0.02(5)

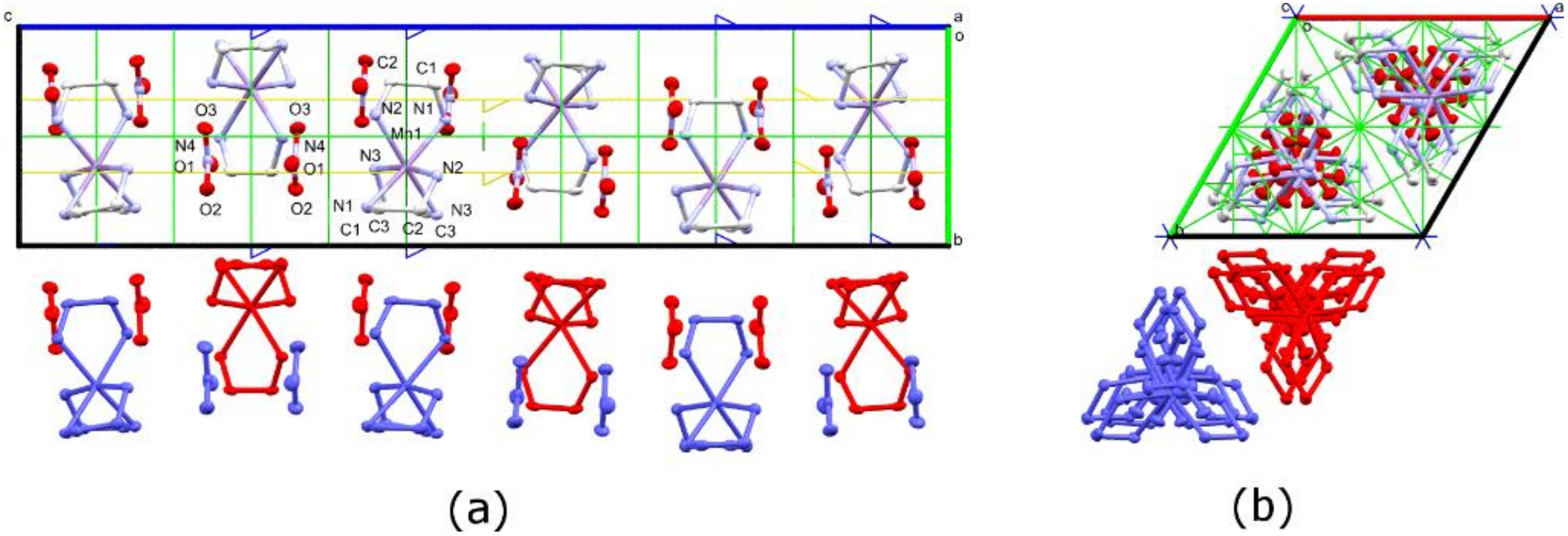
[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [\max(0 \text{ or } F_o^2) + 2(F_c^2)]/3$.

M. Cortijo, A. Valentin-Perez, M. Rouzières, R. Clérac, P. Rosa, E.A. Hillard, *Crystals*, 2020, 10(6), 472 https://doi.org/10.3390/cryst10060472.

Results and discussion

Low temperature phase of $[Mn(en)_3](NO_3)_2$

$[Mn(en)_3](NO_3)_2$ undergoes a phase transition between 298 and 120 K involving a tripling of the *c* axis and the generation of helicity in the columns (similar to the Zn(II) and Ni(II) analogues).



Anisotropic displacment ellipsoid plot (Mercury, 50% probability) of Λ-$[Mn(en)_3](NO_3)_2$ at 120 K as viewed down the (left) *a* crystal axis and (right) *c* crystal axis. Unit cell and symmetry axes are shown, with blue = 6-fold screw, yellow = 3-fold and green = 2-fold. Hydrogen atoms have been omitted for clarity.

No phase transition was detected in $[Co(en)_3](NO_3)_2$ at 120 K.

M. Cortijo, A. Valentin-Perez, M. Rouzières, R. Clérac, P. Rosa, E.A. Hillard, *Crystals*, 2020, 10(6), 472 https://doi.org/10.3390/cryst10060472.

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Results and discussion

Crystallographic data for $[M(en)_3](NO_3)_2$ at 120 K

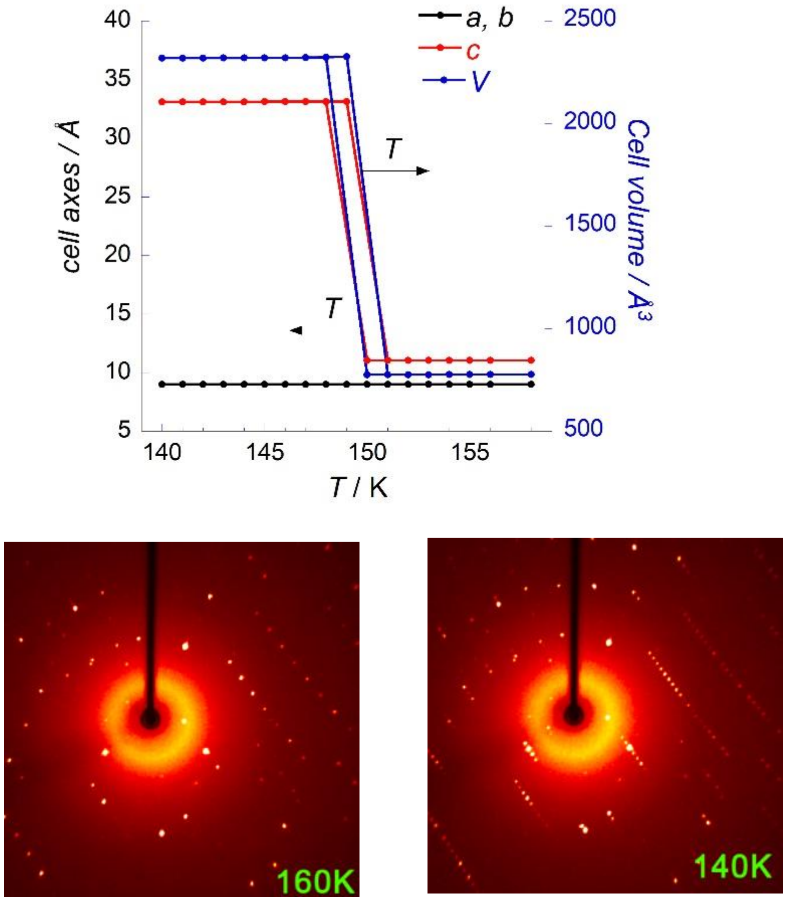
	Δ-Mn	Λ-Mn	Δ-Co	Λ-Co
Formula	$C_6H_{24}MnN_8O_6$	$C_6H_{24}MnN_8O_6$	$C_6H_{24}CoN_8O_6$	$C_6H_{24}CoN_8O_6$
Formula weight	359.25	359.25	363.24	363.26
Crystal system	hexagonal			
Space group	$P6_522$ (no. 179)	$P6_122$ (no. 178)	$P6_322$ (no. 182)	$P6_322$ (no. 182)
a, *b*	8.9999(3) Å	8.9970(3) Å	8.901(2) Å	8.8970(4) Å
c	33.0883(14) Å	33.0623(11) Å	11.065(3) Å	11.0675(4) Å
α, *β*	90°			
γ	120°			
Volume	2321.03(15) Å^3	2317.71(13) Å^3	759.2(3) Å^3	758.70(7) Å^3
Z	6	6	2	2
ρ_{calc}	1.5420 g/cm^3	1.5442 g/cm^3	1.5889 g/cm^3	1.590 g/cm^3
μ (Mo Kα)	0.893 mm^{-1}	0.894 mm^{-1}	1.171 mm^{-1}	1.172 mm^{-1}
Reflections collected	19332 ($5.2° \le 2\theta \le 56.6°$)	33347 ($5.2° \le 2\theta \le 50.7°$)	5187 ($5.3° \le 2\theta \le 50.6°$)	2055 ($5.3° \le 2\theta \le 52.7°$)
Unique	1920 [R_{int} = 0.0300]	1419 [R_{int} = 0.0350]	475 [R_{int} = 0.0285]	522 [R_{int} = 0.0199]
Final *R* indexes [all data]	R_1 = 0.0255 wR_2 = 0.0656	R_1 = 0.0203 wR_2 = 0.0474	R_1 = 0.0163 wR_2 = 0.0444	R_1 = 0.0186 wR_2 = 0.0488
Flack para.	0.04(3)	0.01(3)	0.01(5)	0.006(8)

[a] $R_1 = \Sigma||F_o| - |F_c||/ \Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/ \Sigma[w(F_o^2)^2]]^{1/2}$, $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [\max(0 \text{ or } F_o^2) + 2(F_c^2)]/3$.

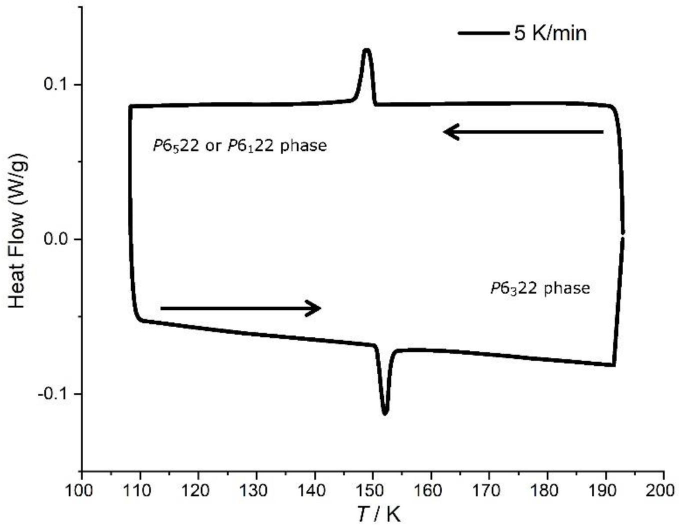
M. Cortijo, A. Valentin-Perez, M. Rouzières, R. Clérac, P. Rosa, E.A. Hillard, *Crystals*, 2020, 10(6), 472 https://doi.org/10.3390/cryst10060472.

Results and discussion

Phase transition in $[Mn(en)_3](NO_3)_2$ at 150(2) K



(top) Cell axes and volume as a function of temperature measured by X-ray diffraction between 158 and 140 K on a single crystal of $[Mn(en)_3](NO_3)_2$; (bottom) Diffraction images of $[\Lambda\text{-}Mn(en)_3](NO_3)_2$ at 160 and 140 K showing tripling of the Bragg peaks at LT.



Differential scanning calorimetry trace for a powder sample of $[Mn(en)_3](NO_3)_2$, scan rate 5 K/min. Top: cooling cycle; bottom: heating cycle.

M. Cortijo, A. Valentin-Perez, M. Rouzières, R. Clérac, P. Rosa, E.A. Hillard, *Crystals*, 2020, 10(6), 472 https://doi.org/10.3390/cryst10060472.

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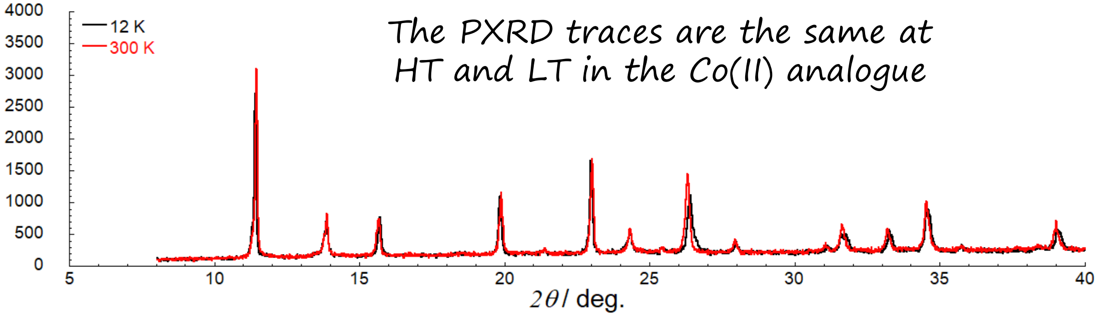
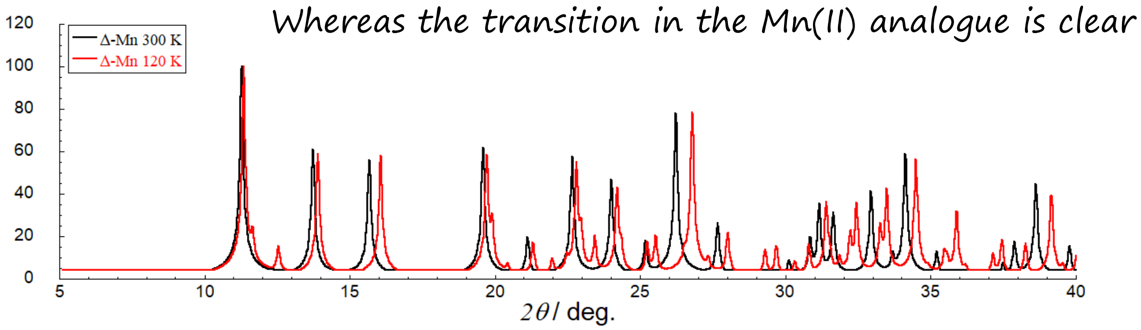
Results and discussion

Absence of phase transition in $[Co(en)_3](NO_3)_2$



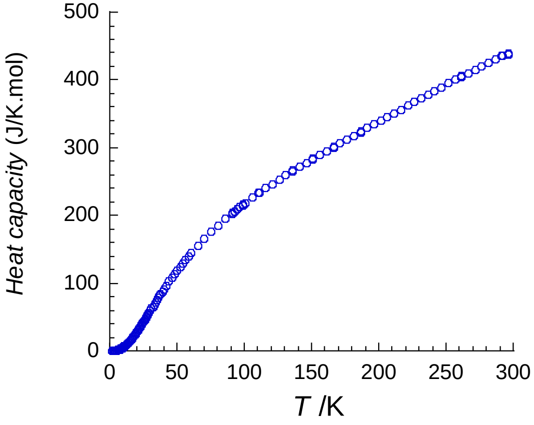
The PXRD traces are the same at HT and LT in the Co(II) analogue



Whereas the transition in the Mn(II) analogue is clear

(top) Powder X-ray diffractograms for $[Co(en)_3](NO_3)_2$ at 12 and 300 K showing no change with temperature; (bottom) Powder diffractograms simulated from Δ-$[Mn(en)_3](NO_3)_2$ single crystal data at 120 and 300 K, which demonstrate the expected change upon the phase transition.

The featureless curve is taken as evidence for the lack of phase transition down to 2 K.



Heat capacity trace for a polycrystalline sample of $[Co(en)_3](NO_3)_2$.

M. Cortijo, A. Valentin-Perez, M. Rouzières, R. Clérac, P. Rosa, E.A. Hillard, *Crystals*, 2020, 10(6), 472 https://doi.org/10.3390/cryst10060472.

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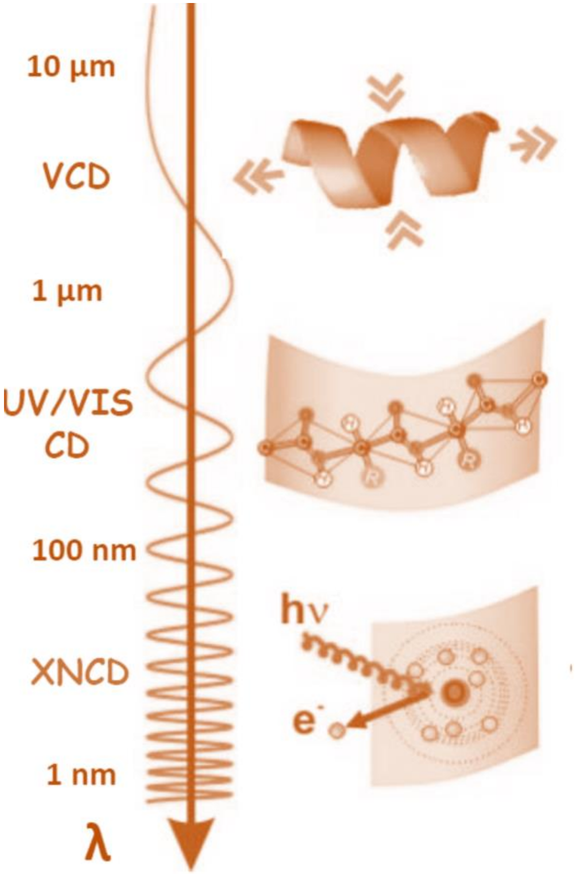
Results and discussion

X-ray natural circular dichroism (XNCD)



- Difference of absorption spectra using right and left circularly polarized X-rays
- Metal K-edge probes the 1s → 3d/4p transitions
- Oriented samples are required (single crystals, among 13 crystal classes)
- No birefringence effects, element specific and orbital selective
- It can only be performed at 3rd generation synchrotron sources

XNCD first measured at the ESRF ID12 in 1998

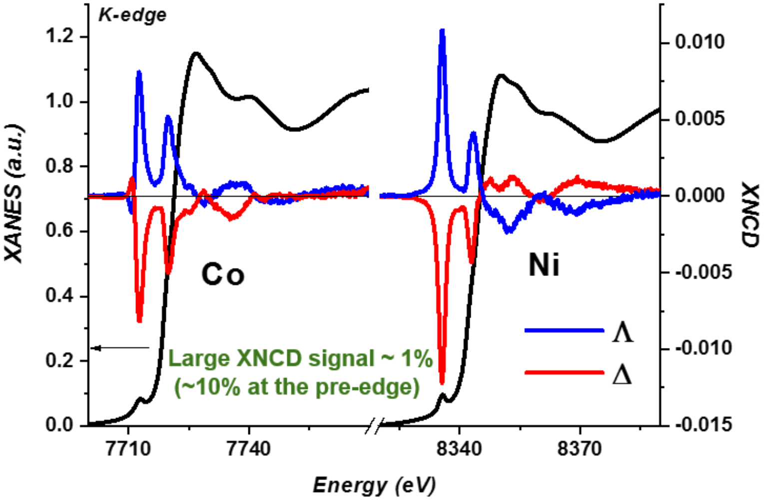
L_1, L_2, and L_3 edges of iodine in α-$LiIO_3$: J. Goulon, et al., *J. Chem. Phys.*, 1998, **108**, 6394.
L_3 edge of $Na_3Nd(digly)_3 \cdot 2NaBF_4 \cdot 6H_2O$; L. Alagna, et al., *Phys. Rev. Lett.*, 1998, **80**, 4799.

Results and discussion

XNCD of $[Co(en)_3](NO_3)_2$ and $[Ni(en)_3](NO_3)_2$

Performed on single crystals at room temperature at the ID12 of the ESRF

Mirror-image CD in the X-ray range, with intense pre-edge features



XNCD (blue and red lines) and X-ray absorption near edge spectra (XANES, black lines) spectra for $[Co(en)_3](NO_3)_2$ and $[Ni(en)_3](NO_3)_2$.

- Selecting crystals for this experiment was difficult, as the chirality of each crystal had to be determined by a full crystallographic data collection.
- Furthermore, we noticed that it was challanging to select a crystals of the Δ enantiomorph of the cobalt compound, suggesting unexpected enantiomeric enrichment (ee).
- How can we test this hypothesis by determining the crystalline ee in a conglomerate mixture?

M. Cortijo, A. Valentin-Perez, A. Rogalev, F. Wilhelm, Ph. Sainctavit, P. Rosa, E.A. Hillard, *Chem. Eur. J.*, 2020, https://doi.org/10.1002/chem.202001783

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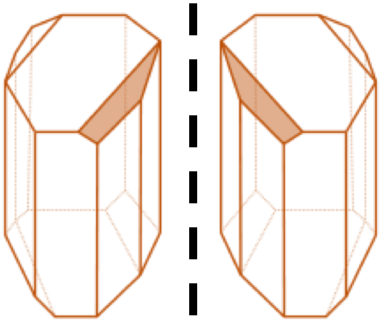
Results and discussion

Methods for determining individual crystal chirality in a conglomerate assembly

1. Visual inspection *requires hemihedry*



Sodium ammonium salt of racemic acid crystallizes as a mixture of two chiral crystal forms related by a mirror image

2. Polarized optical microscopy *requires cubic, transparent crystals*

Enantiomorphic sodium chlorite crystals under POM *(photo from the thesis of Manon Schlindler, University of Rouen, 2019)*.

3. X-ray crystallography *time and labor intensive, impratical for the determination of the handedness of a statistically relevant number of crystals*

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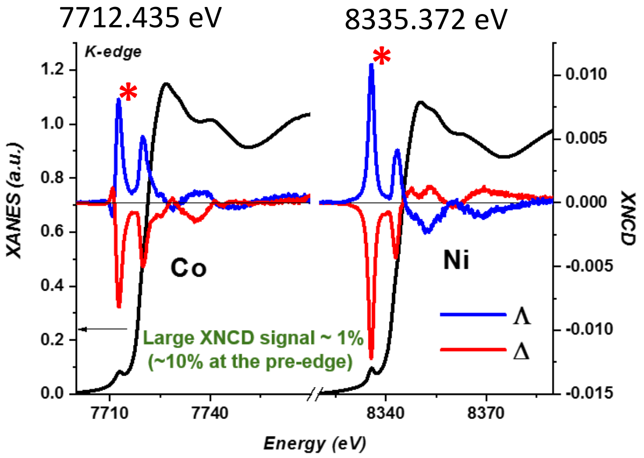
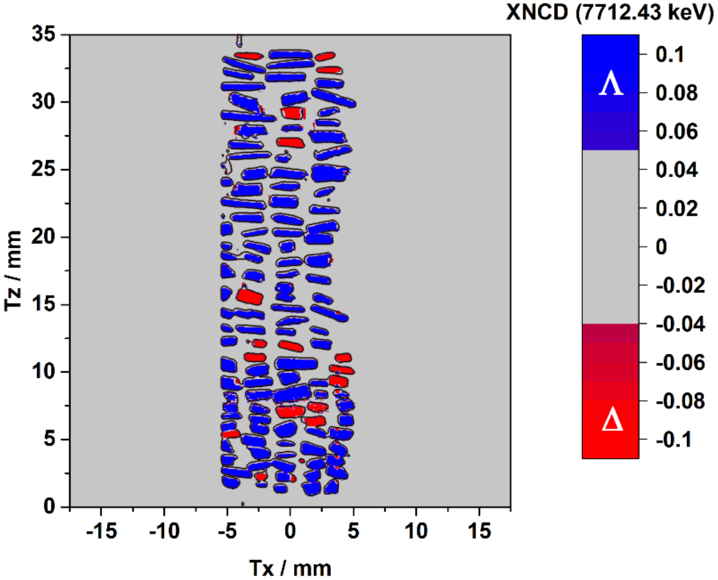
Results and Discussion

XNCD mapping

The X-ray energy was set to the energy corresponding to the maximum XNCD signal and passed over the sample plate while switching polarization, thus giving a negative or positive differential response





Cobalt: crystalline ee 67±13% (Λ-isomer)

The unexpected enantiomeric excess was thought to be due to the influence of ascorbic acid, a chiral natural product, which was added to the reaction as an anti-oxidant.

M. Cortijo, A. Valentin-Perez, A. Rogalev, F. Wilhelm, Ph. Sainctavit, P. Rosa, E.A. Hillard, *Chem. Eur. J.*, 2020, https://doi.org/10.1002/chem.202001783

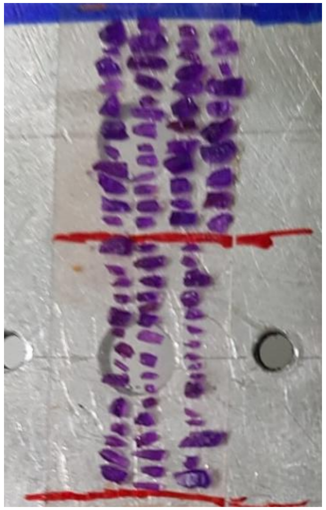
Results and Discussion

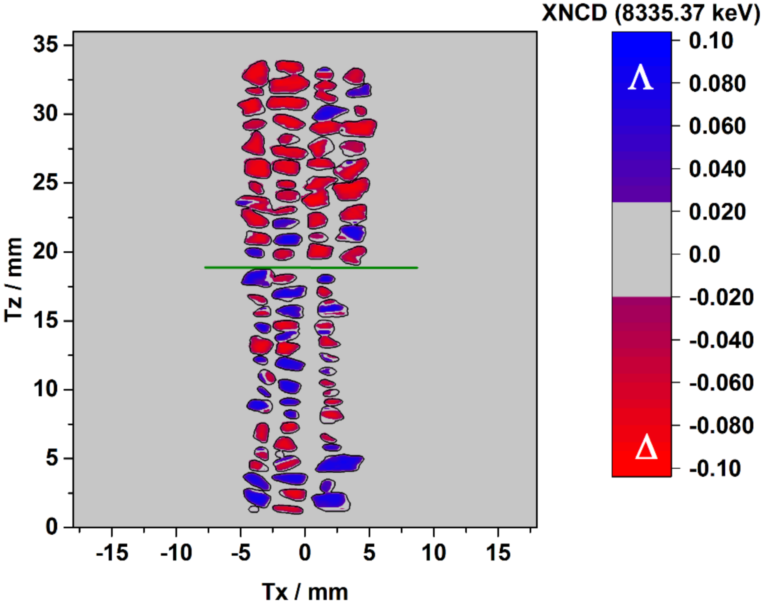
XNCD mapping

To confirm the effect of ascorbic acid, we mapped the nickel derivative in the presence and absence of the additive.

Ascorbic acid added

Ascorbic acid not added





The presence of ascorbic acid results in enantiomeric excess for both compounds:

Cobalt: ee 67±13% (Λ-isomer)

Nickel: ee 65±22% (Δ-isomer)

Nickel: no ee in the absence of ascorbic acid

Ascorbic acid drives enantiomeric enrichment, but in opposite directions for the Co(II) vs. the Ni(II) compound.

M. Cortijo, A. Valentin-Perez, A. Rogalev, F. Wilhelm, Ph. Sainctavit, P. Rosa, E.A. Hillard, *Chem. Eur. J.*, 2020, https://doi.org/10.1002/chem.202001783

Conclusions

- $[Mn(en)_3](NO_3)_2$ and $[Co(en)_3](NO_3)_2$ have been crystallographically characterized for the first time, and were found to be isostructural to the known Zn(II) and Ni(II) analogues, crystallizing as conglomerate mixtures.
- The Mn(II) analogue shows a phase transition at 150(2) K, while no such transition is observed for the Co(II) derivative.
- The Ni(II) and Co(II) enantiomers show mirror-image X-ray natural circular dichroism signals with intense pre-edge features.
- The energy of the pre-edge XNCD peaks was used to map the crystal handedness of an assembly of crystals.
- Ascorbic acid has a differential effect on the complexes, resulting in an enrichment of the Λ isomer for the Co(II) analogue and the Δ isomer for the Ni(II) analogue.

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The authors declare no conflict of interest.

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