Thermo and pressure induced valence tautomerism in layered Mn(II) – nitronyl nitroxide radical compounds: Synthesis, structure, magnetism and Raman spectroscopy

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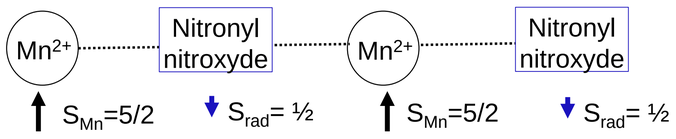
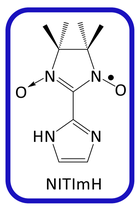
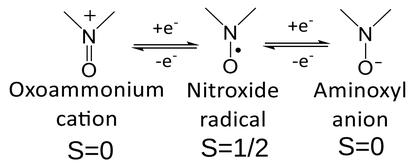
INTRODUCTION

- Elaboration of **molecule-based magnets**: magnetic molecular entities
- Alternation of different spin with **antiferromagnetic interactions**: non-zero magnetization
- Metal – radical synthesis approach:
- Mn^{2+}: 5 free e^-, high spin
- Free radical:

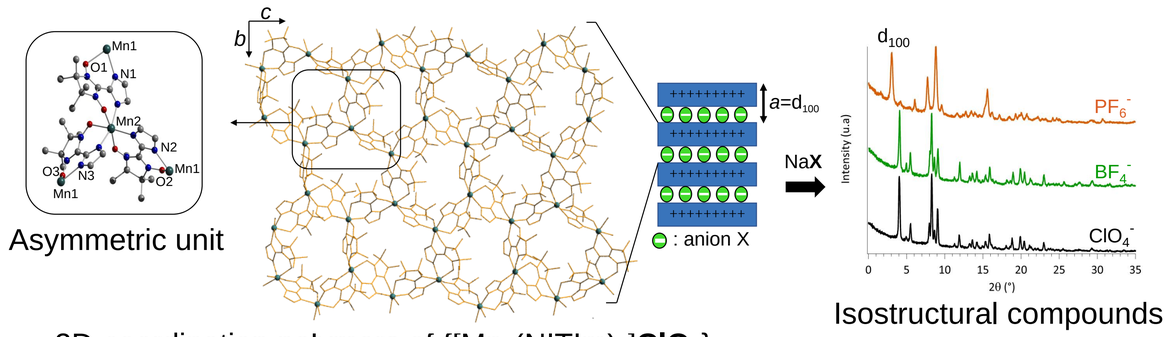




- Stable: delocalization unpaired electron on two NO
- Chelating and bridging ligand
- Non-innocent: spin carrier
- Redox active species



SYNTHESIS AND X-RAY STRUCTURE



- 2D-coordination polymers of $\{[Mn_2(NITIm)_3]\mathbf{ClO_4}\}_n$
- Honeycomb structure along *a* axis
- Variable counter-anions

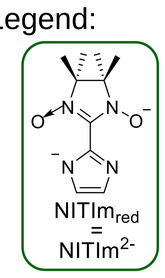
MAGNETIC PROPERTIES – VALENCE TAUTOMERISM

- Thermo-induced electrons transfer: **Valence tautomeric conversion**
- Transfer from metallic cations to radicals
- Counter-anion X impacts on transition temperature and mechanism: modification of interlayered interactions and radical delocalization

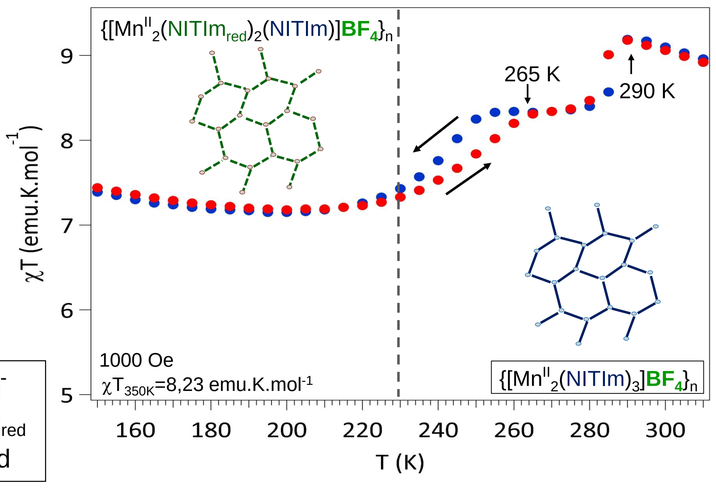
- **Oxidation**: $Mn^{2+} \rightarrow Mn^{3+}$ and **reduction**: $NITIm^- \rightarrow NITIm_{red}$ (**2/3** of the radicals)

$$\{[Mn^{II}_2(NITIm)_3]\mathbf{X}\}_n \underset{T\uparrow}{\overset{T\downarrow}{\rightleftharpoons}} \{[Mn^{III}_2(NITIm_{red})_2(NITIm)]\mathbf{X}\}_n$$

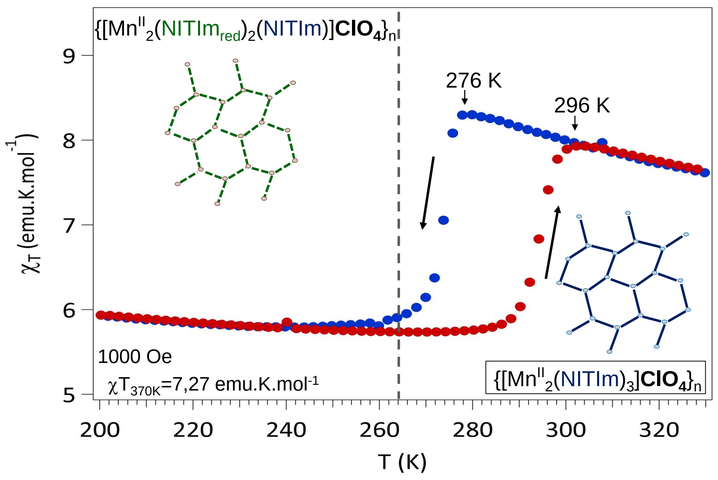
Legend:



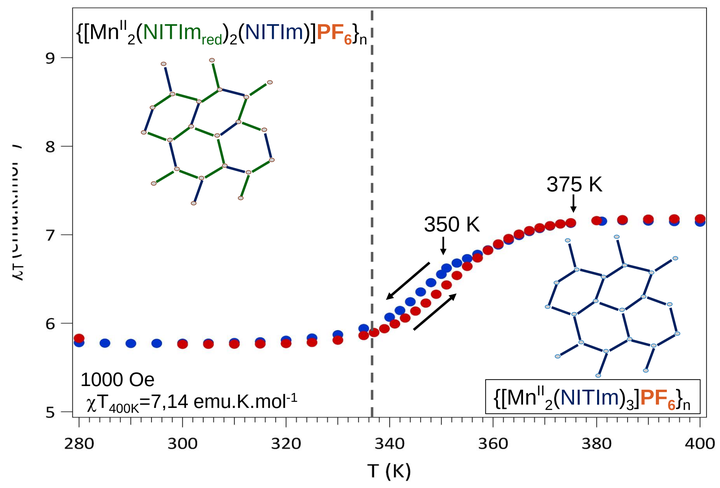
: Mn^{2+} — : $NITIm^-$
: Mn^{3+} — : $NITIm_{red}$
dotted: delocalized



- 1/3 of the radicals are **delocalized** at low T
- Middle interactions between polymers

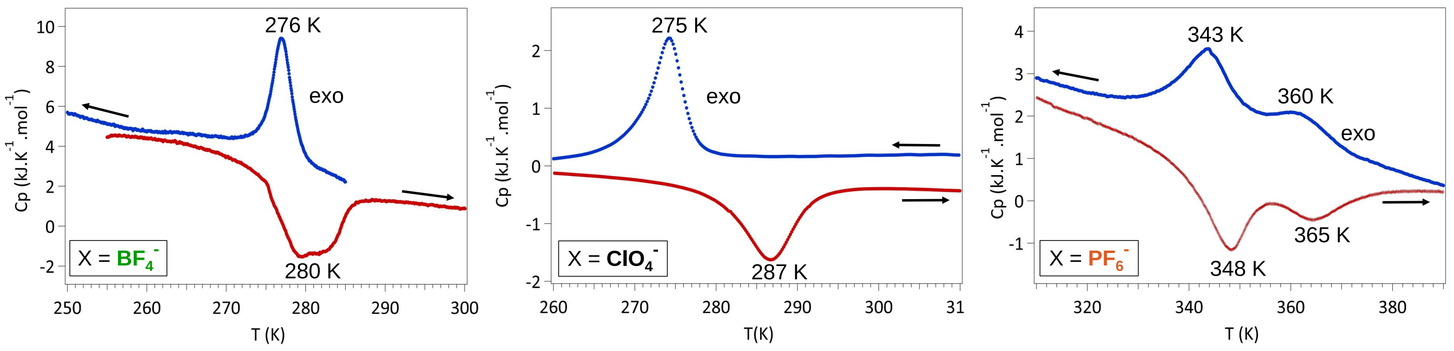


- 1/3 of the radicals are **delocalized** at low T
- Strong interactions between polymers



- 1/3 of the radicals are **localized** at low T
- Weak interactions between polymers

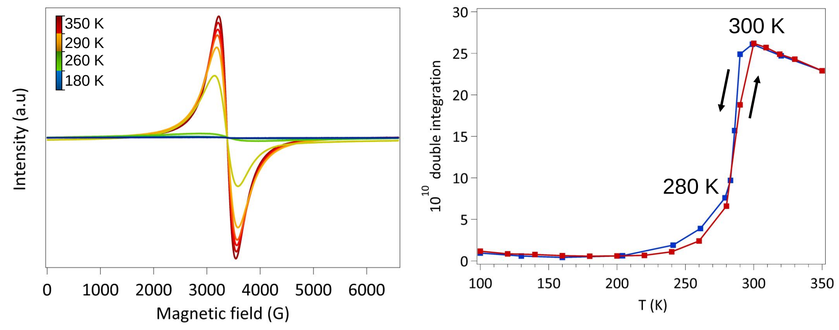
DIFFERENTIAL SCANNING CALORIMETRY



- In agreement with magnetic susceptibility
- $X = \mathbf{BF_4^-}$ and $\mathbf{PF_6^-}$: two dependent peaks ⇔ two successive Mn^{2+} oxidation

ELECTRON PARAMAGNETIC RESONANCE

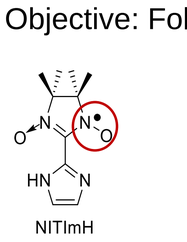
- $\{[Mn_2(NITIm)_3]\mathbf{BF_4}\}_n$



- Heating: $Mn^{3+} \rightarrow Mn^{2+}$
- Double hysteresis

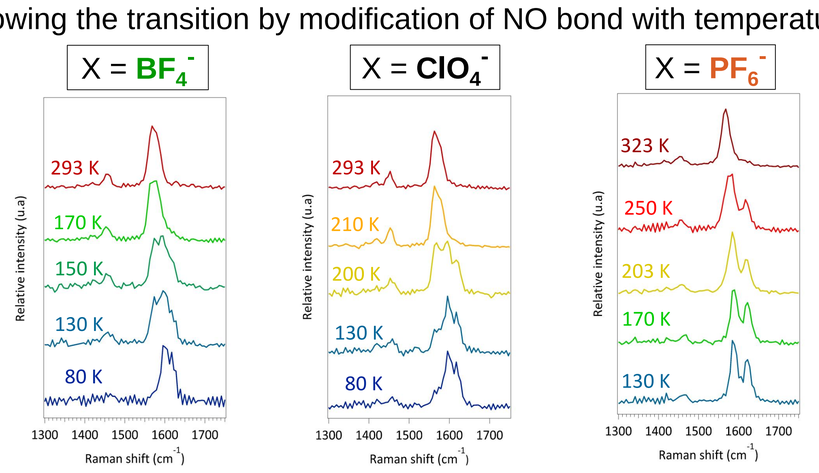
RAMAN SPECTROSCOPY AT VARIABLE T

- Objective: Following the transition by modification of NO bond with temperature



Elongation
υ=1500-1600 cm^{-1}

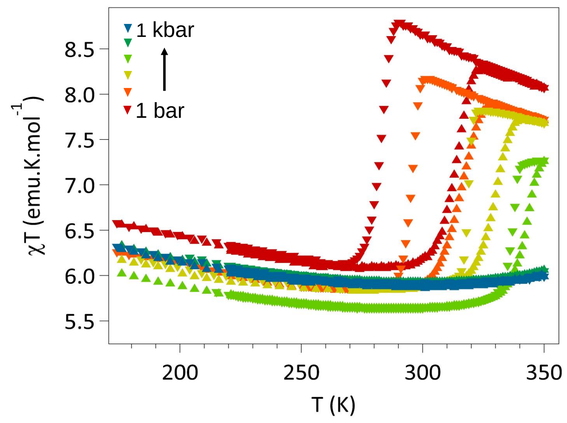
NITImH Raman signature

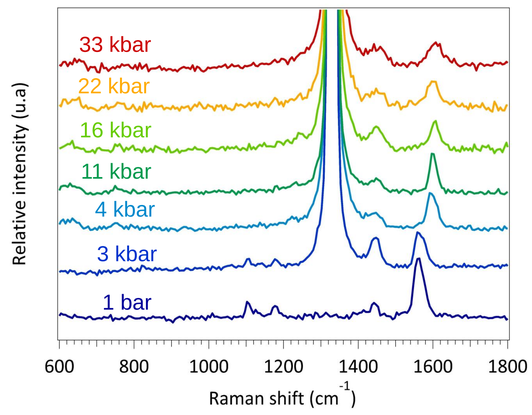


- For $X = \mathbf{BF_4^-}$ and $\mathbf{ClO_4^-}$:
  - υ(NO·) = 1570 cm^{-1} at 293 K
  - Broadband between 200 K and 130 K
  - 2nd peak at 80 K: υ = 1620 cm^{-1}
  - ➔ Delocalization and strong interactions
- For $X = \mathbf{PF_6^-}$:
  - υ(NO·)= 1570 cm^{-1} at 323 K
  - 2nd peak at υ = 1620 cm^{-1} increases and decreases clearly with T
  - ➔ Localization and weak interactions

MAGNETISM AND RAMAN SPECTROSCOPY UNDER P

- Anisotropic pressure on $\{[Mn_2(NITIm)_3]\mathbf{ClO_4}\}_n$ powder





- Hydrostatic high pressure CuBe cell
- Transition shifts to higher temperature
- Hysteresis loop is compressed
- Diamond anvil cell
- Transition at 4 kbar: 1560 ➔ 1610 cm^{-1}
- Reversible

X-ray at variable T: $V_{Mn^{2+}\text{-rad}}$= 2037,5 Å^3 —P→ $V_{Mn^{3+}\text{-rad reduced}}$= 1974,1 Å^3

➔ **Pressure favorizes the valence tautomerism conversion**

CONCLUSION

- Switchable ferrimagnetic compounds: thermo-induced valence tautomeric conversion
- Structural modification with different counter-anions: modification of transition temperature and inter-layered interactions
- Raman spectroscopy: new band at 1620 cm^{-1} (NO· reduction)
- Pressure favorizes VT phenomenon

Future: conductivity measurement, X-ray under pressure, new anions…

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