

Metal-radical frameworks memories

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Coordination chemistry of nitronyl nitroxide free radicals has played a major role in the development of molecular-based magnetic materials. Even today, the metal-nitroxide bond remains a singular source of very diverse and original magnetic systems [1].

With nitronyl nitroxide (NIT) wearing imidazole groups (ImHR), we synthesized layered compounds $\{[\text{Mn}_2(\text{NITImR})_3]\text{X}\}_n$, in which positively charged 2D manganese-radical coordination polymers alternate with layers of anions X^- [1-3]. Some compounds exhibit thermo-induced valence tautomerism (VT) due to electron transfer between the manganese ions and radicals (fig.1 left) [2]. Some other, compounds do not exhibit valence tautomerism but behave as ferrimagnets (fig. 1 right), with T_C near 50 K [3].

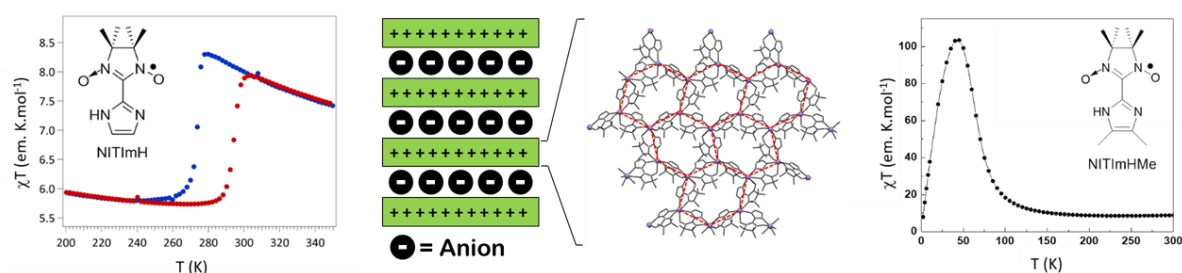


Fig. 1: Temperature dependence of χT for $\{[\text{Mn}_2(\text{NITIm})_3]\text{ClO}_4\}_n$ and $\{[\text{Mn}_2(\text{NITImMe})_3]\text{ClO}_4\}_n$

In this presentation, we show either how magnetic properties of these systems can be adjusted using anions or substituents on the radical or by applying pressure. We also explore how these adjustments are related to the interaction and cooperativity between the layers of the Mn(II)-radical polymers, and the potential for achieving 3D frameworks.

References

- [1] D. Luneau *Eur. J. Inorg. Chem.*, **2020**, 2020, 597-604 DOI: 10.1002/ejic.201901210
- [2] C. Lecourt, Y. Izumi, L. Khrouz, F. Toche, R. Chiriac, N. Bélanger-Desmarais, C. Reber, O. Fabelo, K. Inoue, C. Desroches, D. Luneau *Dalton Trans.*, **2020**, 49, 15646-15662 DOI : 10.1039/d0dt03243c
- [3] E. Yörük, C. Lecourt, D. Housset, Y. Izumi, W. L. Ling, S. Kodjikian, E. Tretyakov, K. Inoue, K. Maryunina, C. Desroches, H. Klein, D. Luneau *Inorg. Chem. Front.*, **2024**, 12, 328-341 DOI : 10.1039/d4qi02257b