

MS13-2-3 Structural and Magnetic Properties of the Oxalate-Based [Cu^ICr^{III}] Complexes: the Influence of the Tridentate Ligand and Simple Anions
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Abstract

Design of new materials with targeted physical properties is a very attractive field of research nowadays. In recent years, the structural diversity of metal-organic coordination systems has paved the way for the development of multifunctional materials that combine two or more different properties, especially magnetic and electrical ones. A very important role in the design and synthesis of such materials belongs to the oxalate moiety, C₂O₄²⁻, due to its various possibilities of coordination to metal centres and its ability to mediate electronic effects between paramagnetic metal ions. The synthetic strategy for the preparation of (hetero)polynuclear species is "building block chemistry", in which a molecular anionic ligand, very often the tris(oxalato)metallate anion [M^{III}(C₂O₄)₃]³⁻ (M^{III} = Cr, Fe, Ru, Rh, Mn or V), is used as a ligand towards other metal cations. Starting from the same reactants, the structural uncertainty of the obtained coordination compounds can lead to two basic cases: (i) both the structures and the chemical compositions are different; the obtained compounds differ significantly from each other, reflecting the great versatility of a self-assembly system; (ii) the structures are different, but the whole coordination networks have the same chemical composition, when the obtained compounds are classified as supramolecular isomers.[1]

Inspired by the structural versatility of oxalate-based [CuFe] compounds containing 2,2':6',2''-terpyridine (terpy)[2], seven novel oxalate-based [Cu^ICr^{III}] compounds: [Cu₄(terpy)₄Cl₅][Cr(C₂O₄)₃]·9H₂O (1; terpy = 2,2':6',2''-terpyridine), {[Cr₂Cu₄(H₂O)₂(terpy)₄(C₂O₄)₇]·10H₂O}_n (2), [Cr₂Cu₄(H₂O)₂(terpy)₄(C₂O₄)₇]·12H₂O (3), [Cu(H₂O)₃(terpy)]-[CrCu(H₂O)(terpy)(C₂O₄)₃]₂·9H₂O (4), [Cu(H₂O)(terpy)(NO₃)]-[CrCu(H₂O)(terpy)(C₂O₄)₃]·6H₂O (5), [CrCu₂(terpy)₂(C₂O₄)₃(NO₃)₂]·1.5H₂O·CH₃OH (6) and [Cr₂Cu₄(H₂O)₄(terpy)₄(C₂O₄)₆]-[Cr₂Cu₂(terpy)₂(C₂O₄)₆]·10H₂O (7) were obtained from the reaction of an aqueous solution of the building block [Cr(C₂O₄)₃]³⁻ and a methanol solution containing Cu²⁺ ions and the terpyridine ligand by the layering technique. Interestingly, changing only the anion of the starting salt of copper(II), NO₃⁻ instead of Cl⁻, resulted in an unexpected change in the bridge type, oxalate (compounds 2–7) versus chloride (compound 1), which affected the overall structural architecture. Compounds were studied by single-crystal X-ray diffraction, IR spectroscopy, magnetization measurements and density functional theory (DFT) calculations.

References

- [1] J.-P. Zhang, X.-C. Huang and X.-M. Chen, Supramolecular isomerism in coordination polymers, *Chem. Soc. Rev.*, 2009, 38, 2385–2396.
[2] L. Kanižaj, D. Barišić, F. Torić, D. Pajić, K. Molčanov, A. Šantić, I. Lončarić and M. Jurić, Structural, Electrical, and Magnetic Versatility of the Oxalate-Based [CuFe] Compounds Containing 2,2':6',2''-Terpyridine: Anion-Directed Synthesis, *Inorg. Chem.*, 2020, 59, 18078–18089.