

1D-Coordination Polymers and Discrete Complexes With {LnCu₅}³⁺ Metallamacrocycles Demonstrating Single Molecule Magnet Behavior or Magnetocaloric Effect

Anna Pavlishchuk¹, Matthias Zeller², Eva Rentschler³, Fabrice Pointillart⁴, Anthony W. Addison⁵

¹Purdue University, L. V. Pisarzhevskii Institute of Physical Chemistry, ¹Purdue University, ³Johannes Gutenberg University, ⁴The University of Rennes 1, Rennes. ⁵Drexel University
apavlish@purdue.edu

Utilization of the building block approach can result in formation of coordination polymers and polynuclear discrete complexes with interesting functional properties (i.e. magnetic and luminescent properties, catalytic activity, and in the case of porous structures – selective sorption of different substrates). In the majority of cases the properties of final assembly are in large parts defined by the properties of building blocks, which makes the choice of the initial blocks very important.

Here, heteropolynuclear copper(II)-lanthanide(III) 15-metallacrowns-5 were used as the initial building blocks. Hexanuclear

{LnCu₅}³⁺ 15-metallacrowns-5 are metallamacrocyclic complexes constructed from five repeating -[Cu-N-O]- fragments with an additional lanthanide(III) ion at the center of the complex. 15-Metallacrowns-5 are of particular interest for molecular magnetism because they provide a nearly ideal pentagonal equatorial environment for the Ln(III) ion which, in combination with appropriate apical coordination, can result in a D_{5h} geometry, which is favorable for quenching of quantum tunneling and can potentially lead to large energy barriers.

Series of discrete complexes and 1D-coordination polymers were obtained from metathesis reactions of anions in initial building blocks [LnCu₅GlyHA₅]₂(SO₄)₃ (GlyHA²⁻ is the dianion of glycinehydroxamic acid; Ln³⁺ = Gd³⁺, Dy³⁺ and Ho³⁺) with different polycarboxylates or mononuclear anionic complexes and the crystal structures of the resulting complexes were determined by single crystal X-Ray diffraction.

The magnetic properties of the obtained assemblies are mainly governed by the exchange interactions within initial metallacrown units [LnCu₅GlyHA₅]³⁺. The *dc* magnetic properties for obtained complexes reveal presence of ferromagnetic exchange interactions between Ln(III) and Cu(II) ions in {LnCu₅}³⁺ (Ln³⁺ = Gd³⁺, Dy³⁺ and Ho³⁺), while exchange interactions between adjacent Cu(II) ions in metallamacrocyclic cores are antiferromagnetic.

The *ac* studies for complexes with {DyCu₅}³⁺ and {HoCu₅}³⁺ units demonstrate temperature and frequency dependencies of out-of-phase signals evidencing for SMM behavior. The 1D-coordination polymer {[Ho-MC]₂(p-bdc)₂(p-bdc)}_n obtained from terephthalate (p-bdc²⁻) demonstrates slow magnetic relaxation below 20.5 K and possesses a comparatively high value for the anisotropic barrier U_{eff} (101 K). 1D-polymers built from

{GdCu₅}³⁺ units and [Crox₃]³⁻ or [Cuox₂]²⁻ (ox = oxalate) demonstrate a significant magnetocaloric effect (ΔS= 24.26 J·K⁻¹·Kg⁻¹ (5 K, 13 T) and ΔS= 24.26 J·K⁻¹·Kg⁻¹ (5 K, 13 T)).

Acknowledgement: AVP thanks Purdue's Ukrainian Scholars Initiative, Department of Chemistry and Jean Chmielewski for providing support and the opportunity to conduct research at Purdue University.