

RATIONAL DESIGN OF SINGLE MOLECULE MAGNETS WITH THIOSEMICARBAZONE LIGANDS

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In memoriam to Prof. Mihail Revenco

The coordination chemistry of the transition metal complexes containing thiosemicarbazide derivatives are investigated due to their attractive chemical, physical and biological properties. Using various thiosemicarbazide derivatives and different metal ions with a in different oxidation states, allows the preparation of a large number of coordination compounds with original structures and properties.

In this work we present a new area of activation of the thiosemicarbazide fragment and its condensation product with salicylaldehyde - thiosemicarbazone by coordination with manganese metal ions. It is known that the manganese chemistry with thiosemicarbazide-based ligands is not so much investigated. Recently we described an original template reaction of salicylaldehyde S-alkyl-isothiosemicarbazones with 2-formylpyridine molecules which opens an original synthetic approach to design new families of ligands derived from thiosemicarbazide and, hence, new metal-ion coordination complexes [1]. Manganese(II) is not know to be an efficient templating ion for this type of condensation. Nevertheless using Mn(II) precursors, we were able to successfully synthesize polynuclear manganese complexes. The single crystal X-ray study of these compounds shows the formation of deca- and hexa- nuclear manganese species containing two different ligands: one initial ligand, and the second is the additional product between 2-formylpyridine and salicylaldehyde S-methyl-isothiosemicarbazone.

The non alkylated salicylaldehyde thiosemicarbazone in strongly alkaline solutions allows the formation of the compounds with composition Mn(L)·3H₂O. The X-ray investigation of its structure demonstrated the formation of a binuclear complex of the composition [(MnL₂)(Mn(H₂O)₄)]·2H₂O. The investigation of the magnetic properties of the manganese(II) dimer shows antiferromagnetic interactions between paramagnetic centers. The compound is not soluble in any solvent in inert atmosphere. In the presence of the air oxygen, in methanol solutions the oxidation of the of Mn(II) to Mn(III) and an oxidative dimerization of the coordinated salicylaldehyde thiosemicarbazone anion were detected. As a result, the formation of a new hexadentate bicompartimental ligand coordinated to two different manganese(III) ions by O₂N₄ donor atoms has been observed. The manganese(III) units [(Mn₂L)(CH₃O)₂(CH₃OH)₂] are assembled in polymer *via* μ₂-oxo bridges provided by methoxy groups coordinated to the metal ions. Low-temperature magnetic investigations of the polymer indicates a ferromagnetic interaction and a slow relaxation in *ac* susceptibility, confirming the SMM behavior of the complexes.

- [1] Mihail D. Revenco, Oleg V. Palamarciuc, Paulina N. Bourosh, Janusz Lipkowski, M.Gdanec, Yurii A. Simonov, Rodolphe Clérac, *Inorganica Chimica Acta* 368, **2011**, p. 157–164.