

MANGANESE - PROMOTED OXIDATIVE DIMERIZATION OF THE SALICYLALDEHYDE THIOSEMICARBAZONE: STRUCTURE AND MAGNETIC STUDIES

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The coordination compounds of the 3d-elements containing the thiosemicarbazide fragment as ligand possess important biological and physical proprieties. The manganese chemistry of the thiosemicarbazone derivatives is not much investigated.

The salicylaldehyde thiosemicarbazone is usually a tridentate ligand coordinating using the O,N,S-set of donor atoms as neutral molecule H₂L, monoanion HL⁻ or dianion L²⁻.

It is also known that the salicylaldehyde thiosemicarbazone prefer to form with 3d element compounds in neutral or basic forms of the ligand. If the reaction is developed in the presence of the air oxygen, under these conditions the manganese(II) ions undergo usually an oxidation. To protect the oxidation the interaction of the salicylaldehyde thiosemicarbazone was investigated under inert atmosphere. In these conditions a new family of manganese dimer coordination compound with the general formula [(MnL₂)(Mn(H₂O)₄)]·2H₂O (see figure 1a) have been synthesized and characterized.

This type of compounds is not soluble in any solvent in inert system. In presence of the air oxygen, in different solvents they undergo a series of oxidative transformations. In methanol solutions the salicylaldehyde thiosemicarbazone undergoes a dimerisation via sulphur atoms and form a -S-S- bound. As a result, a new hexadentate di-compartmental ligand is formed. The manganese ions are oxidized to +3 oxidation state. Each newly formed ligand is coordinated to two manganese(III) ions. The manganese(III) units are assembled in polymer via μ₂-oxo- bridge, provided by two coordinated methoxy groups. The coordination polyhedra of the central atom is completed with a methanol molecule coordinated in axial position. The general formula of these compounds is [(Mn₂L)(CH₃O)₂(CH₃OH)₂]_n (Fig. 1b).

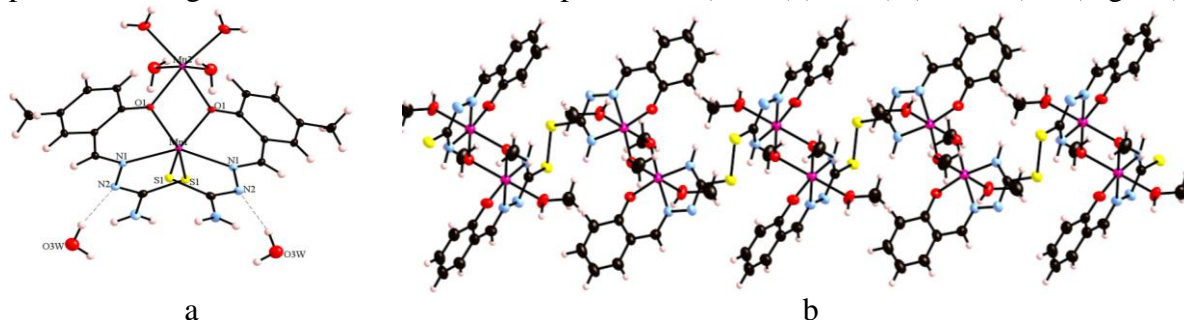


Fig. 1. ORTEP representation of the manganese coordination compounds with salicylaldehyde thiosemicarbazone

The magnetic proprieties of the manganese(II) dimer compound show an antiferromagnetic interaction between paramagnetic centers. In the case of manganese(III) polymers the magnetic susceptibility shows a ferromagnetic coupling at low temperature and the slow relaxation in ac susceptibility confirming the nature of the single molecule magnets.