# Solvothermal Syntheses, Crystal Structures of Two New Thioantimonates(III) of the $Mn_2(L)Sb_2S_5$ Family with L = Diethylenetriamine and *N*-Methyl-1,3-Diaminopropane and a Study of the Magnetic Properties of Four Compounds of the Series

L. Engelke[a], R. Stähler[a], M. Schur[a], C. Näther[a], W. Bensch[a], R. Pöttgen[b], and M. H. Möller[b]

[a] Institut für Anorganische Chemie, Olshausenstraße 40, D-24118 Kiel, Germany
[b] Institut für Anorganische und Analytische Chemie, Wilhelm Klemm Straße 8, D-48149 Münster, Germany

Reprint requests to Prof. Dr. Wolfgang Bensch. Fax: +49(0)431 880 1520.
E-mail: wbensch@ac.uni-kiel.de

Z. Naturforsch. **59b,** 869 – 876 (2004); received March 26, 2004

The two new compounds $Mn_2(L)Sb_2S_5$ (L = diethylenetriamine = DIEN, N-methyl-1,3-diaminopropane = MDAP) were prepared under solvothermal conditions using the elements as starting materials. Both compounds crystallise in the monoclinic space group $P2_1/c$ with the lattice parameters $a = 10.669(7)$, $b = 12.805(2)$, $c = 12.072(1)$ Å, $\beta = 115.786(7)^\circ$, $V = 1485.1(4)$ Å$^3$ for L = DIEN and $a = 10.1859(7)$, $b = 12.7806(6)$, $c = 12.1256(8)$ Å, $\beta = 110.173(8)^\circ$, $V = 1481.7(2)$ Å$^3$ for L = MDAP and $Z = 4$. The primary building units are $SbS_3$ pyramids, $MnS_6$ and $MnS_4N_2$ distorted octahedra. These primary building blocks are interconnected to form $Mn_2Sb_2S_4$ hetero-cubane units. The hetero-cubanes share common corners, edges and faces thus forming a second hetero-cubane. These secondary building units are joined to form layers within the (100) plane. The connection mode yields ellipsoidal pores within the layers. The amines are exclusively bound to one of the two crystallographically independent $Mn^{2+}$ cations and they point into the pores and between the layers separating the layers from each other. The interlayer separation and the size of the pores depend on the sterical requirements of the amine incorporated into the network. A pronounced distortion of the $MnS_4N_2$ octahedron results from a significant elongation of one Mn-S distance from 2.866 Å (L = methylamine, MA) to 3.185 Å for L = MDAP. The magnetic susceptibility curves are typical for low-dimensional antiferromagnetic materials and the large negative values for the Weiss constant $\Theta$ indicate strong antiferromagnetic exchange interactions. The magnetic properties are significantly influenced by the change of the Mn-S bonds introduced by the different amines. The compounds decompose at elevated temperatures with a two step reaction for L = MA and ethylenediamine and in a one step reaction for the bidentate acting amine molecules.

*Key words:* Solvothermal Synthesis, Thioantimonates, Crystal Structures, Magnetic Properties, Thermal Decomposition