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From an Organic-Functionalized Ge_4S_6 Cage to a Chalcogenidometallate Organic Coordination Framework with Antiferromagnetic Chain Behavior

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The interest in open framework compounds containing chalcogenide building units is due to the intrinsic combination of porosity with further specific chemical or physical properties of the chalcogenide moiety.[1–7] To date, three different classes of these compounds have been introduced in which chalcogenidometallate complexes or clusters are linked 1) by chalcogenide ligands as in the open framework based on $[Cu_5In_{30}S_{54}]^{13-}$ clusters,[8] 2) by metal ions as observed in $[Sn(Zn_4Sn_4S_{17})]^{6-}$,[9] or 3) by coordinating amines as in $[Zn_8S(SC_6H_5)_{14}{\cdot}C_{13}H_{14}N_2]$.[10] The last group represent inorganic–organic hybrid frameworks that add the peculiarities of an organic linker—such as flexibility, chirality or further donor/acceptor capabilities—to the characteristics of the metal chalcogenide fragment—such as optoelectronic properties or magnetism.

Based on the directed synthesis of organic-functionalized chalcogenidometallate complexes, which we have reported very recently,[11,12] we present a new class of inorganic–organic hybrid compounds, in which inorganic chalcogenidometallate cages (Ge_4S_6) with donor groups (COO^-) at covalently bonded terminal organic ligands are linked by the coordination of transition-metal ions (Mn^{2+}).

The thiogermanate organic coordination framework, $[Mn_2\{(OOCC_2H_4Ge)_4S_6\}(MeOH)(dmf)_2]$ (**1**), was synthesized by reaction of the fourfold propionic acid substituted adamantane-type thiogermanate $(HOOCC_2H_4Ge)_4S_6$ (H_4PAGeS, Figure 1a) with $MnCl_2{\cdot}4H_2O$ under solvothermal conditions as colorless crystals (Figure 1b, c). The structure was determined by single-crystal X-ray diffraction[13,14] and the complex was also characterized by elemental analysis.

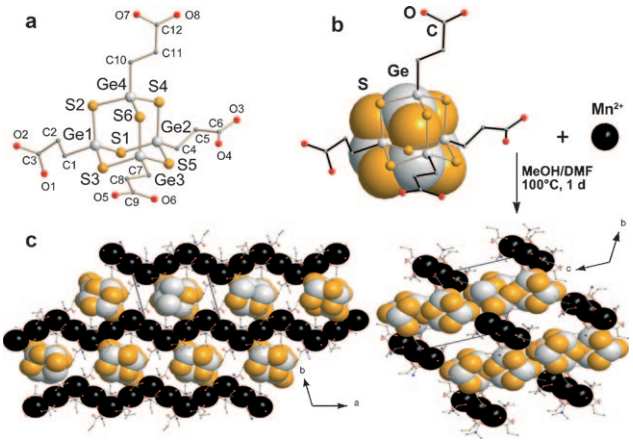

Figure 1. a) Molecular structure of a H_4PAGeS building unit (H atoms not shown). b) Sketch of the reaction $H_4PAGeS + Mn^{2+}$ (Ge, S and Mn atoms in space filling representation) to give c) the three-dimensional framework of **1**, viewed along 001 (left) and 100 (right).

Each asymmetric unit of **1** contains one $[(OOCC_2H_4Ge)_4S_6]^{4-}$ (PAGeS) adamantane cage, two Mn^{2+} ions (on three crystallographic sites), one coordinated methanol and two coordinated DMF molecules. The PAGeS cage is linked to eight Mn atoms (Figure 2a): the propionic acid substituent at Ge1 coordinates to three Mn (Mn1–Mn3) atoms at once in a η^2-μ,μ bridging mode, whereas the COO^- group at Ge2 is just a monodentate ligand to Mn2 with the second O atom (O4) being uniquely non-coordinating. The two donor atoms at each of the ligands at Ge3 and Ge4 serve to connect Mn1 with Mn2. Hence, the three crystallographically independent Mn atoms exhibit different local coordination environments (Figure 2b). Mn1 is octahedrally coordinated by one of the O atoms of six different PAGeS

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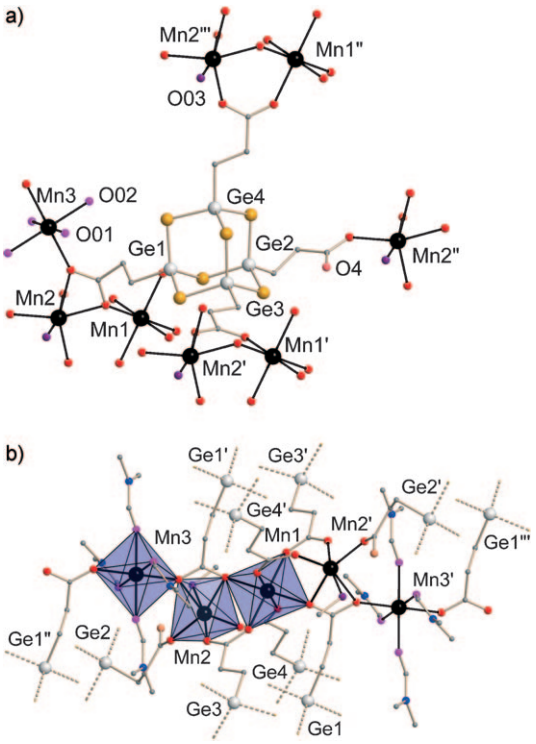

Figure 2. a) Coordination of the PAGeS unit to eight Mn^{2+} ions. b) Coordination environments of the three Mn centers by O donor atoms of COO^- groups (red), DMF (pink) or MeOH molecules (violet).

complexes, which are in turn linked by this single metal atom, whereas the second O atoms of the same COO^- groups are always involved in further coordination. Mn2 shows a complicated, distorted octahedral coordination by two O atoms of the chelating ligand at Ge1, three further PAGeS in a monodentate fashion, and one MeOH molecule. Mn3 is mono-coordinated by two PAGeS units in *trans*-position and four terminal DMF molecules.

The linkage of PAGeS cages as one secondary building unit (SBU-1) and Mn atoms results in the formation of one-dimensional zigzag chains of corner-sharing $\{MnO_6\}$ units along the crystallographic *a* axis at *a*00, *a*10, *a*01, and *a*11. The PAGeS cages are distributed between the $\{MnO_6\}_x$ chains and bind to four independent zigzag chains each, producing a highly intertwined three-dimensional network. In detail, Mn2, Mn1, and Mn2′ form a carboxylate-bridged, trimeric linear SBU-2, which is bridged by DMF-coordinated Mn3 as a biconnector into the zigzag chain. Beside this linkage, each trimeric SBU-2 binds to eight adamantane SBU-1s to achieve an $8+2=10$ connectivity. Each SBU-1, in turn, is connected to four of the SBU-2 trimeric aggregates. Thus **1** exhibits a novel (4,10)-connected three-dimensional network topology.

UV/Vis spectra served to explore the electronic excitation energy. Figure 3 shows the spectrum that was recorded from a suspension of single crystals of **1** in nujol oil.

In accordance with the colorless crystals, the electronic excitation of **1** is situated in the UV region. However, one

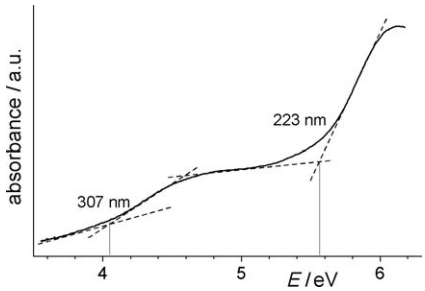

Figure 3. UV/Vis spectrum of **1**, recorded from a suspension of single crystals in nujol oil.

can clearly distinguish between two onsets of absorption (Figure 3). The first (4.04 eV) can be assigned to the p(O)→d(Mn) charge transfer as typical for carboxylate ligated $\{MnO_6\}$ arrangements;[15] the second (5.57 eV) can be assigned to the p(S)→p(Ge) CT excitation, similar to the absorption observed for organic ligated $R_4Ge_4S_6$.[16] This illustrates that the hybrid compound **1** contains different electronic domains. Modifications, such as the use of thiocarboxylate ligands and/or different transition metal atoms, will serve to additionally fine-tune these properties as observed for purely inorganic chalcogenidometallate networks.[5,6]

Magnetic susceptibility measurements have been performed on **1** at 1000 Oe between 1.8 and 300 K. At room temperature, the χT product is 16.7 $cm^3 K mol^{-1}$, in good agreement with the presence of four $S=5/2$ Mn^{II} spins. The value of χT decreases continuously with T to reach 2.85 $cm^3 K mol^{-1}$ at 1.8 K, indicating the presence of dominating antiferromagnetic (AF) interactions along the Mn chain. In order to model the magnetic properties of **1**, the crystal structure was analyzed by localizing the possible magnetic pathways. Three different magnetic interactions were identified along the Mn chain: 1) J_1 between Mn1 and Mn2 bridged by two *syn–syn* carboxylates and μ-O1 (Mn1-O1-Mn2 110.94(18)°); 2) J_2 between Mn2 and Mn3 linked by a single μ-O2 (Mn2-O2-Mn3 138.48(19)°); and 3) J_3 mediated by a single *anti–anti* carboxylate between Mn1 and Mn3. According to the literature,[17] J_1 should represent the strongest AF interaction due to the two *syn–syn* carboxylate bridges, being reinforced by the μ-O1 link. J_2 and J_3 should be much smaller, most likely with $|J_2|>|J_3|$ due to the direct orbital overlap through μ-O2 for J_2 and the *anti–anti* carboxylate bridge for J_3, which is usually extremely weak being ferro- or antiferromagnetic by nature.[17b,18] A simple Heisenberg trinuclear $S=5/2$ model, taking into account only J_1 (with the spin Hamiltonian: $H=-2JS_{Mn1}(S_{Mn2}+S_{Mn2'})$ and neglecting the other pathways (i.e., considering the Mn3 spin as Curie spin), was not able to reproduce the experimental data below 50 K. Therefore, as a second approach the interaction J_1 and J_2 were included in the model (still neglecting the weaker J_3 interaction) as a $J_1J_1J_2J_2$ interaction sequence between $S=5/2$ spins (inset of Figure 4). The following Heisenberg classical spin Hamiltonian was considered [Eq. (1)].

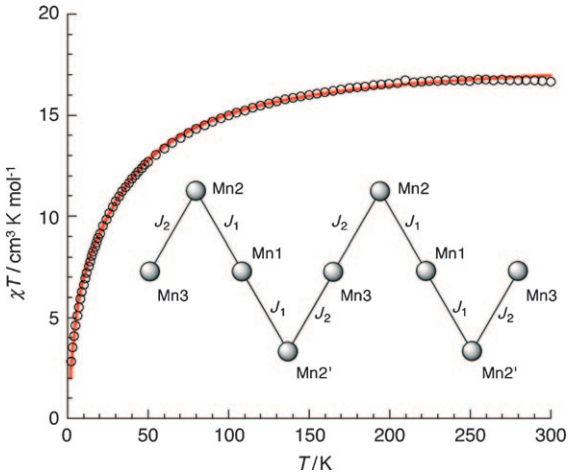

Figure 4. χT vs. T plot for **1** at 1000 Oe (χ: magnetic susceptibility defined as M/H per four Mn^{II} sites). The solid red line is the best fit obtained with the $J_1J_1J_2J_2$ Heisenberg chain model described in the text. Inset: magnetic topology of the Mn chain.

$$H = -2\left\{\sum_{i=0}^{N} J_1(S_{4i+1}\cdot S_{4i+2} + S_{4i+2}\cdot S_{4i+3}) + J_2(S_{4i+3}\cdot S_{4i+4} + S_{4i+4}\cdot S_{4i+5})\right\} \quad (1)$$

The work of Fisher[19] was extended in order to calculate the magnetic susceptibility of this system [Eq. (2)] in which u_i is given by Equation (3).

$$\chi T = \frac{2Ng^2\mu_B^2 S(S+1)}{3k_B}\left[\frac{2(u_1+u_2)+(u_1+u_2)^2+2(1+u_1^2u_2+u_1u_2^2+u_1^2u_2^2)}{1-u_1^2u_2^2}\right] \quad (2)$$

$$u_i = \left(\tanh\left(\frac{2J_iS(S+1)}{k_BT}\right)\right)^{-1} - \frac{k_BT}{2J_iS(S+1)} \quad (3)$$

As shown in Figure 4, an excellent fit of the data is obtained with $J_1/k_B = -2.8(2)$ K, $J_2/k_B = -0.3(1)$ K, and $g = 2.03(5)$. The estimation of the magnetic interactions is in excellent agreement with the previously reported values.[18,19] A more complicated model taking into account J_3 led to an overparametrization of the fit (with multiple solutions) and meaningless magnetic parameters.

In conclusion we have presented a novel type of hybrid compound based on organic-functionalized metalchalcogenide cages as well as transition-metal ions as nodes, both of which contribute to the electronic situation and thus the properties of the network.

Experimental Section

General: All manipulations steps were performed under an Ar atmosphere. All solvents were dried and freshly distilled prior to use. H_4PAGeS was prepared according to the reported method.[12] $MnCl_2{\cdot}4H_2O$ was purchased from Aldrich (>98%) and used as received.

Synthesis of $[Mn_2\{(OOCC_2H_4Ge)_4S_6\}(MeOH)(dmf)_2]$ (1): H_4PAGeS (0.01 g, 0.013 mmol) and $MnCl_2{\cdot}4H_2O$ (0.004 g, 0.0195 mmol) were placed in a pyrex glass tube (10 mm diameter and 200 mm length) in a solvent mixture of DMF/methanol (0.3/0.2 mL). The tube was sealed under vacuum and heated at a constant rate of 1 °C min^{-1} to 100 °C for 24 h, then cooled at a constant rate of 0.5 °C min^{-1} to room temperature. The colorless crystals of **1** were washed with methanol repeatedly (5× 2 mL). Yield: 0.006 g (0.0056 mmol, 43%); FT-IR (KBr, Nujol mull in polyethylene windows): $\tilde{\nu}$ = 3418.1 (br, methanol OH), 2921.7 (w), 1655.5 (s, DMF C=O), 1565.7 (s, COO asymmetric stretch), 1400.3 (s, COO symmetric stretch), 1299.8 (m, CN), 1255.3 (w), 1168.0 (w), 1106.4 (m), 778.9 (m), 709.0 (w), 424.4 (s, GeS), 381.0 (w), 315.0 (w), 195.4 (w), 153.2 cm^{-1} (w); UV/Vis (suspension of single crystals in nujol oil): λ_{max} (ε) = 307-(4.04), 223 nm (5.57 eV); elemental analysis calcd (%): C 21.40, H 3.33, N 2.62, S 17.96; found: C 21.36, H 3.30, N 2.62, S 18.00.

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Keywords: chalcogens · magnetic properties · manganese · organic–inorganic hybrid composites · solvothermal conditions

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[13] Data collection on Stoe IPDS2T ($Mo_{K\alpha}$ radiation, graphite monochromization, $\lambda = 0.71073$ Å, 100 K). Structure solution by direct methods, full-matrix-least-squares refinement on F^2 by using SHELXTL software.[14] $C_{19.09}H_{35.36}Ge_4Mn_2N_2O_{11.59}S_6$ (**1**): triclinic, $P\bar{1}$, $a = 12.311(3)$, $b = 14.049(3)$, $c = 14.181(3)$ Å, $\alpha = 116.92(3)°$, $\beta = 111.72(3)°$, $\gamma = 91.66(3)°$, $V = 1973.6(7)$ Å^3, $Z = 2$. $R1 = 0.0542$ [$I > 2\sigma(I)$], $wR2 = 0.0988$ (all data), GOF = 0.969. For more details, see the Supporting Information. CCDC-746886 contains the supplementary crystallographic data for compound **1** in this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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