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Reactions of H_2S with AgCl within a Porous Coordination Network

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A silver(I) sulfide species is now imbedded in a porous coordination network. Such a composite system builds on the molecule tetrakis(methylthio)-1,4-benzenedicarboxate that holds out the hard carboxylate to europium(III) to form a host net, while taking on AgCl using its soft sulfur side arms. AgCl is then treated with H_2S to form the dark-colored Ag_2S species, while leaving the hard host net intact and upstanding. This hard−soft duality serves to conjoin the rich electronic flavors of metal chalcogenides and the flexible textures of coordination nets.

A major direction in the field of porous coordination networks (PCNs) or metal−organic frameworks (MOFs) is to introduce metal species into the PCN cavities in order to achieve advanced solid-state properties (e.g., heterogeneous catalysis and electroactivity).[1] Because of their widely interesting electroactive and semiconductive properties,[2] it would be especially useful to encapsulate metal chalcogenides within the structurally well-defined PCN matrixes. The fundamental importance of such a task is easy to envision because such chalcogenide−PCN composites are to provide a unique and versatile system for exploring charge-transfer and redox processes within the confinement of these hybrid porous media. Evidently, a continuous domain of chalcogenide thus confined can be likened to a quantum wire; an isolated cluster, a quantum dot. Moreover, synergistic interaction between the chalcogenide species and the PCN host could also create rich potentials for novel properties. For example, the organic-containing PCN host might serve as a photosensitizer for the embedded semiconductive chalcogenide domain and thus could enhance the photoelectrochemical performance.

The making of the chalcogenide−PCN composites is, however, challenging because of the generally low solubility and low volatility of the interested metal chalcogenides (i.e., direct deposition via the vapor or solution phase,[1i−n] as usually employed, is not applicable). It is, therefore, necessary to first introduce into the pores the metal species as a soluble or volatile precursor and then effect the conversion into the desired chalcogenides, e.g., by reaction with H_2S. Unfortunately, MOF systems that exhibit both an effective uptake of metal species and a tolerance toward the harsh treatment of H_2S have, to our knowledge, not been reported.[3] Here we report preliminary studies on a PCN that points to an effective strategy to introduce metal sulfides as guest species and thus to open up a new dimension for functionalization. Specifically, the networks build on the bifunctional molecule H_2TMBD [tetrakis(methylthio)-1,4-benzenedicarboxylic acid; Chart 1],[4]

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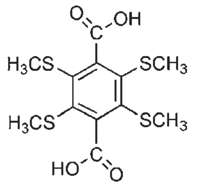
Chart 1



H$_2$TMBD

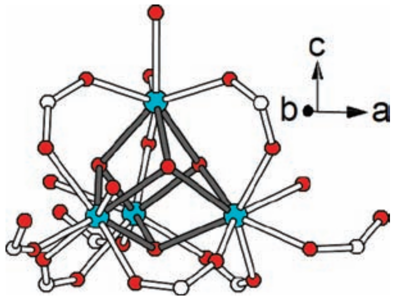


Figure 1. Eu_4O_4 cuboid and associated carboxylate groups and water molecules in **1**. H atoms are omitted. Color code: cyan, Eu; red, O; white, C.

with the chemically hard carboxylates bonding with europium(III) clusters to build up the main framework, while the thioether groups act as donors for the encapsulation of soft guest species like AgCl. Interestingly, the encapsulated metal halides can be reacted with H_2S gas to form sulfide species while maintaining the structural integrity of the host net.

Compound **1** (network composition: $[Eu_4(OH)_4(H_2O)_4]_2(C_{12}H_{12}O_4S_4)_9 \cdot 0.98Ag_6Cl_5$) was solvothermally synthesized using H_2TMBD, $EuCl_3$, and CH_3CN/H_2O (solvents) in the presence of AgCl [see the Supporting Information (SI) for details], with the excess AgCl solid separated from the product via a solvent-based density-discrimination method (by using the high-density solvent CH_2BrCH_2Br) as described in the literature.[5] The crystal structure[6] of **1** is based on C_3-symmetric $Eu_4(OH)_4(H_2O)_4$ "Eu_4O_4" cuboids (Figure 1) interlinked by carboxylate groups of the TMBD molecules to form a 3D network with hexagonal channels (Figure 2). The solvent-accessible region is 26.1% (calculated by the program *PLATON*[7]). Each Eu_4O_4 cuboid is bonded to nine bridging TMBD molecules: three act as individual struts, and the other six divide into three pairs, each acting as a single strut across two Eu_4O_4 cuboids. The Eu_4O_4 cuboid thus serves as a 6-connected node, and its trigonal-prismatic geometry leads to a 6-connected topology (see Figure S1 in the SI) unrelated to the more common α-Po net; this relatively uncommon topology was also documented in other coordination systems.[8] The chemically soft AgCl forms a cyclic trimeric unit Ag_3Cl_3 chelated by three pairs of methylthio groups from a neighboring Eu_4O_4 unit. The Ag_3Cl_3 unit also forms short Cl···O contacts (3.231 Å) with a water O atom from a second Eu_4O_4 unit, indicating hydrogen-bonding interaction. Overall, the Ag_3Cl_3 and two associated Eu_4O_4 units are aligned along the *c* axis (i.e., the channel direction; see Figure 2), and the channels are not blocked by the AgCl units. X-ray structural refinement indicates that the Ag and Cl sites are not fully occupied, with occupancy factors of 0.812 and 0.687 for Ag and Cl, respectively, which is also supported by elemental analyses. The extra positive charge from silver(I) can be balanced by the negative network. The Eu_4O_4 cuboid motif observed here is common for trivalent lanthanoids (Ln) and is often refined as the hydroxo cluster $Ln_4(\mu_3\text{-}OH)_4$.[9] Overall, the formula $[Eu_4(OH)_4(H_2O)_4](C_{12}H_{12}O_4S_4)_{4.5} \cdot Ag_{2.436}Cl_{2.061}$ was crystallographically determined for the network of **1**, with the negative charge (i.e., −0.875 per formula unit) likely balanced by H_3O^+ species [see the SI for details on thermogravimetric (TGA) and elemental analyses]. The partial occupancy of the AgCl sites could be partly due to the low solubility of AgCl and partly due to the stability of the host net of **1** (i.e., the host net can form even without fully occupied AgCl sites). In fact, the host net can be prepared in the absence of AgCl, even though the yield and purity are lower (see **2** in the SI).

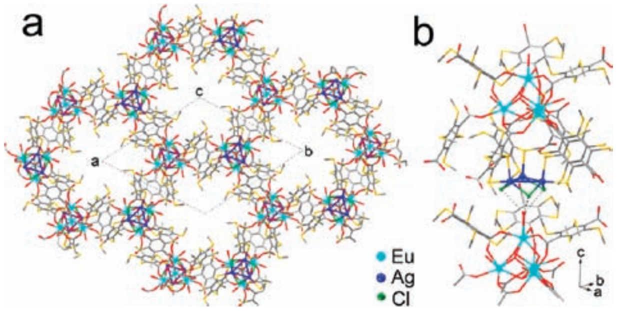


Figure 2. Crystal structure of **1**: (a) view along the channel direction; (b) an Ag_3Cl_3 unit imbedded between two Eu_4O_4 clusters and the associated TMBD molecules. Dotted lines: short distance (3.231 Å) between the O and Cl atoms.

The chloride component also plays an important role in the synthesis. For example, when Cl^- was replaced by the weaker anion NO_3^-, i.e., when $Eu(NO_3)_3$ and the more soluble $AgNO_3$ were used instead, we obtained only one crystalline product of the composition Ag_2TMBD (i.e., without Eu), in which the Ag^+ ion binds both the carboxylate and methylthio groups (see the SI). In other words, the more "naked" Ag^+ of $AgNO_3$ appears more promiscuous; it does not select the thioether group over the carboxylate group. Taken together, AgCl serves to template and promote the host net of **1**. To stick to the main thread of this Communication, we now delve into **1** and the H_2S treatment.

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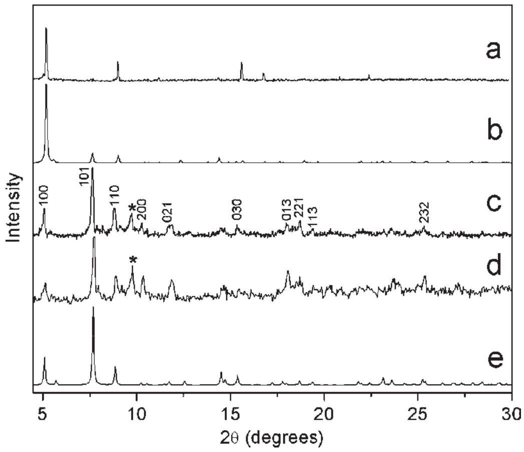

Figure 3. Powder XRD patterns of (a) an as-made sample of **1**; (b) a simulation from the single-crystal structure of **1**; (c) a sample of **1** treated with H_2S for 1 day, (d) a sample of **1** treated with H_2S for 3 days, and (e) a simulation of the Eu-TMBD host net of **1** with Ag atoms around channel centers. The starred peak in parts c and d cannot be indexed and is ascribed to an unknown phase.

Upon exposure to H_2S gas, the colorless crystals of **1** become black (see Figure S2 in the SI for photographs of the crystals), suggesting the formation of Ag_2S-related species (which is also consistent with the X-ray photoemission spectra; see Figure S3 in the SI). Elemental analyses on the sample treated for 3 days indicate a 2:1 ratio between Ag and the incremented S component (i.e., aside from S atoms from TMBD). Elemental analyses also show that over 80% of the Cl component remains in the crystal sample, even though the crystal samples were heated to 150 °C for 6 h under vacuum before elemental analysis. The persistent Cl component suggests that the reaction between H_2S and AgCl here does NOT generate gaseous HCl as a major product and the Cl^- ion presumably remains bonded to the Ag^I ion (e.g., possibly as a chlorosulfide species like Ag_2SCl^-), with the counterions apparently being the H^+ species resulting from the H_2S treatment. In further studies, we will try to unravel the bonding environments of the Ag, S, and Cl atoms in the H_2S-treated sample and to explore the potential use of the Ag−S−Cl species (e.g., ionic conductivity[10]) and the acidic H^+ counterions (e.g., catalytic activities).

Powder X-ray diffraction (XRD) studies (see Figure 3) indicated retention of the original crystal lattice after the H_2S treatment (see patterns c and d in Figure 3) but with significant changes in the relative intensities of the peaks. As shown in pattern e of Figure 3, the intensity change (e.g., the increase of 101 and decrease of 100) can be modeled, in a rough, first-order approximation, by first removing the AgCl components from the crystal structure of **1** and then placing the Ag atoms around the central region of the channels, i.e., at (0.08, 0.08, 0.25) in the unit cell. The XRD studies indicate that the Ag_2S-containing species formed is likely to be located in the central region of the channels. The following message is thus unequivocal: the Eu_4O_4-TMBD host net of **1** maintains the crystalline order even after H_2S induces the drastic transformation and relocation of the silver(I) species.

In conclusion, these preliminary results indicate that the AgCl component incorporated in the host network of **1** can be converted into sulfide (or chlorosulfide) species by treatment with H_2S, while maintaining the crystalline structure of the host net. This process is facilitated by the distinct hard−soft duality of the network system, in which the bona fide hardness of the europium(III) carboxylate links wards off the H_2S impact and thus allows it to specifically target the softer silver(I) species. The generality of the hard−soft approach, as demonstrated here, is underlaid by the large library of similar bifunctional networks potentially accessible with the synthetic arsenal of crystal engineering. Further exercises to tailor the pore features of the crystalline host nets will likely allow for fine-tuning of the size, shape, and distribution of the metal chalcogenide/halide species at the atomistic level, in order to rationally impact the reactivity and material properties associated with the chalcogenide components.

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Supporting Information Available: Crystallographic data in CIF format for **1**, **2**, and Ag_2TMBD, detailed experimental procedures for **1**, **2**, and Ag_2TMBD, TGA and XPS data for **1**, and photographs of crystals of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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