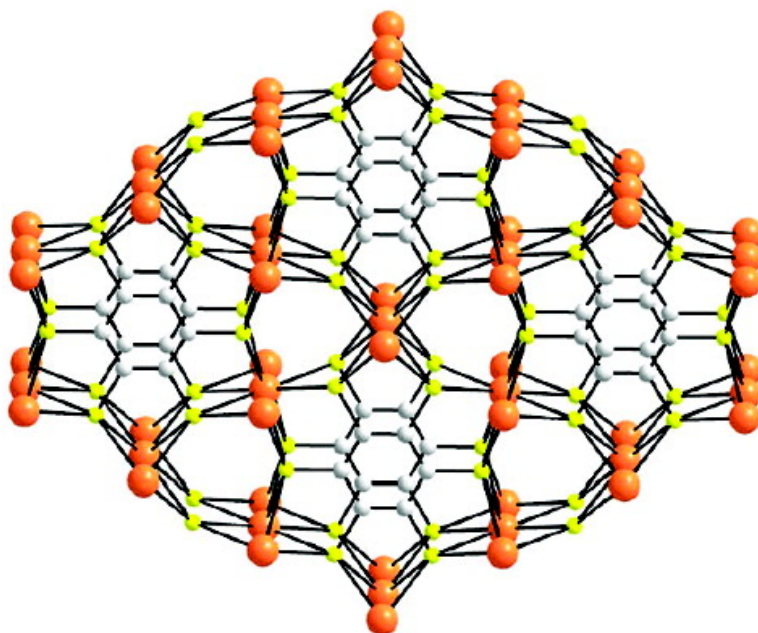


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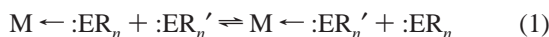
Semiconducting Lead–Sulfur–Organic Network Solids

Dayna L. Turner,[‡] Thomas P. Vaid,^{*‡} Peter W. Stephens,[†] Kevin H. Stone,[†]
Antonio G. DiPasquale,[§] and Arnold L. Rheingold[§]

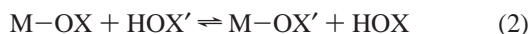
Department of Chemistry and Center for Materials Innovation, Washington University, St. Louis, Missouri 63130, Department of Physics and Astronomy, Stony Brook University, Stony Brook, New York 11794, and Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093

Received September 13, 2007; E-mail: vaid@wustl.edu

Inorganic solid-state compounds constitute the vast majority of well-defined materials with extended bonding in two or three dimensions. However, research over the last two decades has yielded thousands of examples of a new class of crystalline compounds with extended bonding in multiple dimensions: metal ions linked by multidentate, bridging organic ligands.^{1,2} Interestingly, almost all members of this latter class of materials are formed through one of the reactions described by eqs 1 and 2. (Networks built from imidazole³ and triazole,⁴ with their relatively acidic N–H groups, are exceptions.) In eq 1, one metal–ligand dative bond is exchanged for another, and in eq 2, a regular (nondative) covalent metal–oxygen bond is exchanged for another metal–oxygen bond through a protonolysis reaction (or an analogous exchange involving the deprotonated anions; HOX can be an alcohol, carboxylic acid, phosphonic acid, etc.). Many reactions described by eq 1 or eq 2 are fast and reversible at moderate temperatures, and in the synthesis of extended solids, reversibility is critical to the formation of the thermodynamically favored, crystalline phase.



where E = N, O, S, etc.



We are interested in the synthesis of new semiconducting materials, and molecule-based extended solids are an intriguing class of compounds that, with the properly chosen components, may be semiconducting.^{5,6} With covalent bonding throughout the material, they are likely to have the high electron and hole mobilities of traditional inorganic semiconductors, which are $\sim 10^3$ higher than in organic molecular semiconductors, and the molecular components of a molecule-based extended solid would allow the fine-tuning of physical properties that is possible in organic molecular and polymeric semiconductors. Molecule-based extended solids that are analogous to known inorganic semiconductors are a logical starting point. If 1,4-benzenedithiol is considered to be an analogue of H₂S (and $^-SC_6H_4S^- \approx S^{2-}$), the material [Pb(SC₆H₄S)]_n is analogous to PbS, a small-bandgap semiconductor ($E_g = 0.37$ eV).⁷ A similar logic has led others to explore sulfur-based ligands as components of semiconducting networks, including materials based on metal–sulfur dative interactions^{8,9} and a recent report of one-dimensional polymers of Zn and Mn with tetrathioterephthalate.¹⁰ However, in neither case was any electrical conductivity reported. A two-dimensional network containing silver and pyridine-2-thiolate¹¹ and another containing nickel and pyrimidine-2-thiolate¹² are in fact both semiconducting.

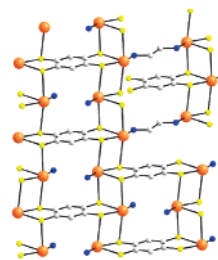


Figure 1. Crystal structure of [Pb₂(S₂C₆H₂S₂(en))_n], determined by synchrotron X-ray powder diffraction. Lead atoms are orange, sulfur yellow, and nitrogen blue.

There are two reports of the synthesis of covalent metal–thiolate network solids, one describing the reaction of several metal precursors with 1,4-benzenedithiol¹³ and the other describing the reaction of several transition metal salts with 1,2,4,5-benzenetetrathiol.¹⁴ In neither case was structural information obtained for materials that were extended in their bonding. It seems that, under properly chosen conditions, a reversible reaction analogous to eq 2, with sulfur substituted for oxygen, would allow the synthesis of crystalline metal–sulfur–organic covalent networks. We have found that a number of metal acetates react with arenepolythiols in refluxing ethylenediamine to yield crystalline metal–sulfur–organic networks. The products from the reactions of Pb(OAc)₂ (OAc = acetate) with 1,4-benzenedithiol, 1,2,4,5-benzenetetrathiol, and benzenehexathiol present a set of contrasting structures and physical properties.

The reaction of 1,2,4,5-benzenetetrathiol and 2 equiv of Pb(OAc)₂ in ethylenediamine (en) at reflux for 16 h gives bright yellow, microcrystalline [Pb₂(S₂C₆H₂S₂(en))_n in 88% yield. The structure was solved by synchrotron X-ray powder diffraction and is shown in Figure 1. Within the extended structure, there are discernible Pb₂C₆H₂S₂Pb “molecular” units, wherein the Pb–S bond distances are 2.58 and 2.62 Å, indicative of regular covalent bonds. Every Pb atom is also coordinated from above and below by sulfur atoms at 2.95 and 3.03 Å (indicating a dative interaction), made possible by an antiparallel alignment with two Pb–S bonds on other Pb₂C₆H₂S₂Pb units. Each Pb is linked to another Pb through a bridging en ligand, leading to an overall square pyramidal S₄N coordination environment for Pb.

The reaction of Pb(OAc)₂ and 1,4-benzenedithiol in a 1:1 molar ratio in ethylenediamine at reflux under N₂ for 16 h gives orange-red, microcrystalline [Pb₃(SC₆H₄S)₃(en)₂]_n in 81% yield. The structure was partially solved by synchrotron X-ray powder diffraction, but the positions of non-Pb atoms were not well-determined and gave unreasonable Pb–S and Pb–N distances. Single crystals suitable for single-crystal X-ray diffraction were grown by treating Pb(OAc)₂ with 1.2 equiv of 1,4-benzenedithiol in unstirred ethylenediamine at 100 °C for 48 h, yielding orange-

[‡] Washington University in St. Louis.

[†] Stony Brook University.

[§] University of California, San Diego.

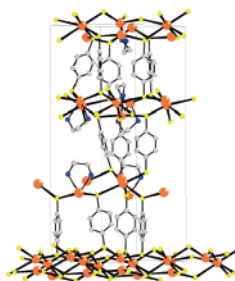


Figure 2. Single-crystal structure of $[\text{Pb}_3(\text{SC}_6\text{H}_4\text{S})_3(\text{en})_2]_n$. Lead atoms are orange, sulfur yellow, and nitrogen blue.

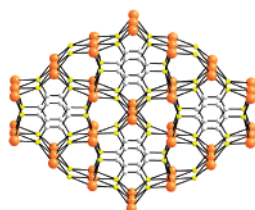


Figure 3. Crystal structure of $[\text{Pb}_3(\text{C}_6\text{S}_6)]_n$, determined by synchrotron X-ray powder diffraction. Lead atoms are orange and sulfur yellow.

red hexagonal and trigonal plates. The single-crystal structure is shown in Figure 2. It consists of layers of Pb atoms in a roughly hexagonal arrangement, with $\text{SC}_6\text{H}_4\text{S}$ units bridging between the layers. There are three inequivalent lead atoms, with Pb(2) coordinated by six sulfur atoms in a distorted octahedral arrangement, Pb(1) coordinated by four S atoms and the two N of a chelating en, and Pb(3) coordinated by three S atoms and the two N of a chelating en. Five of the six inequivalent S atoms are coordinated to two Pb atoms each, with each S having one bond that could be classified as normal covalent (Pb–S distances of 2.745(2)–2.908(2) Å) and one as dative (Pb–S distances of 3.027(2)–3.469(2) Å). The sixth S atom interacts with three Pb atoms at 2.794(2), 3.255(2), and 3.513(2) Å. The difference in length between the longest covalent and shortest dative Pb–S bonds is quite small; the distinction between formally dative and regular covalent Pb–S bonds is somewhat blurred.

The reaction of $\text{Pb}(\text{OAc})_2$ with 0.4 equiv of benzenehexathiols in ethylenediamine at 60 °C for 16 h gives brown $[\text{Pb}_3(\text{C}_6\text{S}_6)]_n$ in 83% yield. Its structure was solved by synchrotron X-ray powder diffraction and is shown in Figure 3. There are layers of Pb atoms and parallel layers of C_6S_6 units in the a – b crystallographic plane. Each sulfur coordinates four Pb atoms, and each Pb is coordinated by eight S atoms. The coordination of Pb is distorted cubic; Pb is at the center of a rectangular prism of eight S atoms with S–S distances of 3.17, 3.47, and 3.96 Å. All Pb–S distances are 3.07 Å. The distinction between regular covalent and dative bonds is completely lost in $[\text{Pb}_3(\text{C}_6\text{S}_6)]_n$, and the bonding is akin to that in an inorganic solid-state compound such as PbS, which has the rock salt structure and in which all Pb–S interactions are equivalent.

The different bonding modes in $[\text{Pb}_2(\text{S}_2\text{C}_6\text{H}_2\text{S}_2)(\text{en})]_n$, $[\text{Pb}_3(\text{SC}_6\text{H}_4\text{S})_3(\text{en})_2]_n$, and $[\text{Pb}_3(\text{C}_6\text{S}_6)]_n$ are reflected in differences in their physical properties. $[\text{Pb}_2(\text{S}_2\text{C}_6\text{H}_2\text{S}_2)(\text{en})]_n$ is composed of molecular units linked by dative bonds, and its visible absorption spectrum indicates a band gap of about 3.1 eV. (Alternatively, the absorption can be considered to be due to a simple ligand-to-metal charge-

transfer transition.) $[\text{Pb}_3(\text{SC}_6\text{H}_4\text{S})_3(\text{en})_2]_n$ has a more extensive network of formally covalent bonds, and there is some ambiguity in classifying its Pb–S bonds as dative or regular covalent, and its visible absorption band edge indicates a band gap of about 2.6 eV. Finally, in $[\text{Pb}_3(\text{C}_6\text{S}_6)]_n$, bonding between the Pb atoms and C_6S_6 groups is similar to that in an inorganic solid-state compound, and its optical band gap is about 1.7 eV. An alternative explanation for the range of band gaps of the three materials is provided by the dimensionality of their Pb–S networks (ignoring the benzene linkages): one-dimensional for $[\text{Pb}_2(\text{S}_2\text{C}_6\text{H}_2\text{S}_2)(\text{en})]_n$, two-dimensional for $[\text{Pb}_3(\text{SC}_6\text{H}_4\text{S})_3(\text{en})_2]_n$, and three-dimensional for $[\text{Pb}_3(\text{C}_6\text{S}_6)]_n$.

Measurements of the pressed-pellet electrical conductivity of $[\text{Pb}_2(\text{S}_2\text{C}_6\text{H}_2\text{S}_2)(\text{en})]_n$ and $[\text{Pb}_3(\text{SC}_6\text{H}_4\text{S})_3(\text{en})_2]_n$ show that both have conductivities of less than $10^{-12} \Omega^{-1} \text{cm}^{-1}$. In contrast, the pressed-pellet conductivity of $[\text{Pb}_3(\text{C}_6\text{S}_6)]_n$ at 22 °C is approximately $2 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$. Variable-temperature measurements of the conductivity of $[\text{Pb}_3(\text{C}_6\text{S}_6)]_n$ follow Arrhenius behavior, with an activation energy of 0.37 eV (see Supporting Information). Doped $[\text{Pb}_3(\text{C}_6\text{S}_6)]_n$ was synthesized by performing the synthesis with a mixture of ~99:1 $\text{Pb}(\text{OAc})_2$ and $\text{Tl}(\text{OAc})$, and the doped material had a conductivity of $1 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$. Attempts to synthesize doped versions of $[\text{Pb}_2(\text{S}_2\text{C}_6\text{H}_2\text{S}_2)(\text{en})]_n$ and $[\text{Pb}_3(\text{SC}_6\text{H}_4\text{S})_3(\text{en})_2]_n$ gave products with electrical conductivities of less than $10^{-12} \Omega^{-1} \text{cm}^{-1}$. However, preliminary experiments show that a selenium analogue, $[\text{Pb}_3(\text{SeC}_6\text{H}_4\text{Se})_3(\text{en})_2]_n$, was dopable by both Tl and Bi and yielded materials with the low but measurable conductivity of $4 \times 10^{-11} \Omega^{-1} \text{cm}^{-1}$. Experiments are underway to examine the electrical transport properties of these semiconducting materials more thoroughly and to synthesize new materials of this type.

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Supporting Information Available: Synthetic details, visible absorption spectra, Rietveld refinement fits, and crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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