

## A Semiconductive Coordination Network Based on 2,3,6,7,10,11-Hexakis(methylthio)triphenylene and BiCl<sub>3</sub>

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Received June 8, 2004

**ABSTRACT:** The reaction of 2,3,6,7,10,11-hexakis(methylthio)triphenylene (**1**) with BiCl<sub>3</sub> in benzene forms near-quantitatively the crystalline composite **1**·BiCl<sub>3</sub>, which is an air stable semiconductor with an electronic band gap of 2.0 eV (diffuse reflectance data). The crystal structure of **1**·BiCl<sub>3</sub> [crystal data: C<sub>48</sub>H<sub>48</sub>S<sub>12</sub>Cl<sub>6</sub>Bi<sub>2</sub>, triclinic, *P* $\bar{1}$ , *a* = 7.7535(3) Å, *b* = 13.8362(5) Å, *c* = 14.0188(5) Å,  $\alpha$  = 107.763(1)°,  $\beta$  = 98.730(1)°,  $\gamma$  = 97.020(1)°, *V* = 1392.76(9) Å<sup>3</sup>, and *Z* = 1] features a composite one-dimensional BiCl<sub>3</sub> framework in which the Bi(III) center is chelated to the organic ligand. The chelation bonds facilitate the ligand–metal center interaction and generate substantial charge transfer phenomena. The ease of crystallization is ascribed to the relatively weak Bi(III)–Cl bonds that serve to connect the organic ligands and the similar crystalline packing motifs of the reactant (**1**) and the product (**1**·BiCl<sub>3</sub>). The synthesis of compound **1**·BiCl<sub>3</sub> indicates that semiconductive networks can be effectively accessed by linking electroactive organic ligands through intervening metal halide moieties. Compound **1**·BiCl<sub>3</sub> can also be made in a solvent-free solid state reaction.

In the field of extended coordination frameworks,<sup>1–5</sup> it is of great interest to access systems with tunable conducting/semiconducting properties.<sup>1,6–10</sup> Among the rapidly growing number of reported coordination networks, the organic ligands are usually of low electroactivity, and their electronic communications with the metal centers are quite weak. As a result, most of the reported coordination networks are insulators, while conductive or semiconductive systems<sup>1,6–10</sup> are relatively rare. To enhance the solid state electroactivity, it is desirable to use electroactive organic ligands that can provide significant electronic interactions with metal centers. For example, a well-known electrically conducting network was based on the coordination between copper(I) iodide and the highly electron deficient ligand 2,5-dimethyl-N,N'-dicyanoquinonediimine,<sup>11</sup> and subsequent studies on similar systems have been reported rather extensively.<sup>7,12,13</sup> More recently, redox active ligands have been equipped with chelating sites with the purpose of promoting stronger metal–ligand interactions. In a commonly studied system, the ligand contains the electron-rich tetrathiafulvalene (TTF) as the core and the tertiary phosphine groups as the chelation sites.<sup>14–18</sup> Such an organic building block is also designed to accommodate wider chemical modifications and should provide flexible control of the prospective metal–organic frameworks as functional electronic materials.

The chelation of organic ligands such as the phosphines with metal ions is, however, in general rather robust, which often makes it difficult to obtain crystalline extended networks. For example, most of the above-mentioned phosphinotetrathiafulvalene complexes were obtained as discrete molecular species rather than extended frameworks.<sup>19–22</sup> In addition, the TTF fragment tends to be quite air sensitive, and this will likely limit the potential application of the resultant solid state material.

In this paper, we report a crystalline framework that may help address, to some degree, the above issues of crystallization and air stability. The structure is based on

the coordination between bismuth trichloride (BiCl<sub>3</sub>) and the polycyclic aromatic ligand 2,3,6,7,10,11-hexakis(methylthio)triphenylene (**1**), and it has the formula of **1**·BiCl<sub>3</sub>. The single-crystal structure<sup>23</sup> of **1**·BiCl<sub>3</sub> features a one-dimensional BiCl<sub>3</sub> framework that is periodically modified by the organic ligand (see Figure 1, especially panel a). In other words, the Bi<sup>3+</sup>–Cl bonds thus constitute an essential link between the organic ligands. Because metal–halogen interactions such as the Bi(III)–Cl bonds are relatively weak (as compared with chelating interactions, for example), they open up a more reversible pathway to build up the extended structure, facilitating the formation of crystalline products. In fact, hybrid frameworks containing chelation ligands and metal–halide linkages have been widely reported,<sup>24–30</sup> as is illustrated by the hundreds of structures uncovered by a search of the Cambridge Structural Database (see the Supporting Information for the search query). Our focus here is to use air stable polycyclic aromatic ligands such as **1** to improve the electroactivity as well as the air stability of the resultant hybrid framework. In addition, a multidentate ligand such as **1** can potentially incorporate more inorganic components [note that in **1**·BiCl<sub>3</sub>, only one of the three bis(methylthio) chelating units of **1** are bonded to the Bi<sup>3+</sup> center] and lead to open frameworks of higher dimensionality.

Although both reactants (**1** and BiCl<sub>3</sub>) are almost colorless, the composite **1**·BiCl<sub>3</sub> is dark red, suggesting effective electronic communication between the organic molecule and the metal center. Diffuse reflectance measurement of the solid sample of **1**·BiCl<sub>3</sub> indicated an electronic band gap of 2.0 eV (Figure 2).<sup>31</sup> Moreover, this hybrid semiconductor is stable to air and its synthesis is straightforward: It can be made in near-quantitative yields using either an organic solvent like benzene or simply by heating a solid mixture of molecule **1** and BiCl<sub>3</sub>.<sup>32</sup>

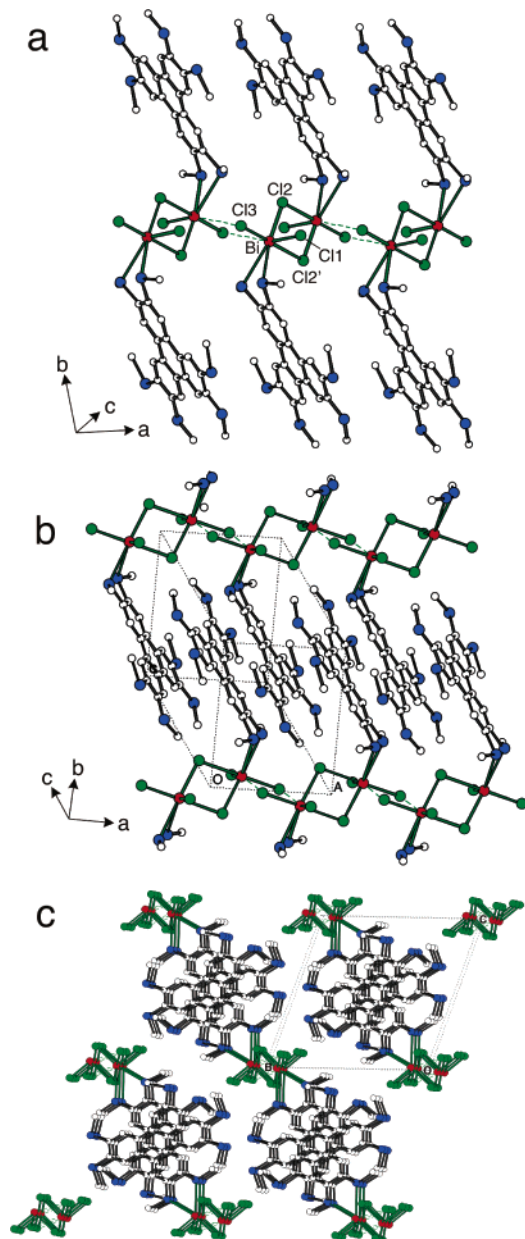
The connectivity of the BiCl<sub>3</sub> chain can be seen in Figure 1a. Each Bi atom is bonded to three crystallographically inequivalent chlorine atoms (Cl1, Cl2, and Cl3). Among these, Cl1 is terminal (Bi–Cl1 length, 2.48 Å); Cl2 is shared by two neighboring Bi atoms (bond lengths: Bi–Cl2, 2.67 Å; Bi–Cl2', 2.92 Å), linking the neighboring BiCl<sub>3</sub> units into distinct centrosymmetric dimers. Such dimeric units of Bi<sub>2</sub>Cl<sub>6</sub> are then connected into an infinite chain through

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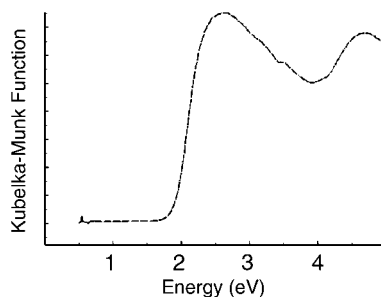
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**Figure 1.** Single-crystal structure of  $1 \cdot \text{BiCl}_3$  (red, Bi; green, Cl; blue, S; and white, C). (a) A chain of  $\text{BiCl}_3$  with each bismuth center chelated to a molecule of **1**. (b) Two of the above chains interdigitate and form a stack of **1** along the *a*-axis. (c) View along the *a*-axis.



**Figure 2.** Room temperature optical absorption spectrum for  $1 \cdot \text{BiCl}_3$ .

the sharing of Cl3 atoms; the two Bi–Cl3 distances (2.58 and 3.27 Å) are rather different, and the longer one can be considered a secondary bond (Bi $\cdots$ Cl van der Waals distance > 3.8 Å<sup>33</sup>). Overall, each Bi atom is surrounded by

five Cl atoms, and they constitute a highly distorted square pyramid with Cl2 at the apex. The open space opposite the apex is occupied by two chelating sulfur atoms from molecule **1** (Bi–S distances, 3.01 and 3.25 Å), which completes a 7-fold Bi coordination resembling a capped trigonal antiprism. The two chelating sulfur atoms thus couple the Bi(III) centers to the triphenylene  $\pi$ -system of **1**, and the  $\text{BiCl}_3$  chain can be considered as being modulated by the organic  $\pi$ -systems in a periodic fashion. The remaining four sulfur atoms from **1** are not bonded to the Bi atom and therefore do not increase the dimensionality of the coordination framework—it remains one-dimensional. Overall, Figure 1a shows a composite structure resembling a double-sided comb, where the inorganic ( $\text{BiCl}_3$ ) spine is flanked by two rows of parallel organic  $\pi$ -planes.

The composite chains interact with each other through interdigitation of the pendant aromatic molecules (Figure 1b), which thus become closely stacked in the face-to-face orientation. Within the stack, two interplanar distances (3.34 and 3.45 Å) are found between neighboring molecules, and the two distances alternate along the stacking direction (the *a*-axis). Viewed on a global scale (Figure 1c), the interdigitation of the aromatic molecules organizes the individual composite chains into layers parallel to the [011] plane. As also seen in Figure 1c, the symmetric shape of molecule **1** imparts a rather smooth curvature surrounding each stack of organic molecules. Such stacks of organic molecules interact with one another through van der Waals contacts and constitute the matrix phase in which the inorganic components ( $\text{BiCl}_3$ ) are dispersed as isolated columns.

It is informative to compare the crystal structure of complex  $1 \cdot \text{BiCl}_3$  with that of molecule **1**. As shown in Figure 1b and Figure S3a (Supporting Information), molecules of **1** in both structures are stacked in the face-to-face manner. The relative orientations of neighboring molecules are similar, although the two interplanar distances (3.44 and 3.43 Å) in **1** are slightly different from those of  $1 \cdot \text{BiCl}_3$  (3.34 and 3.45 Å). A comparison of Figures 1c and S3b also reveals the similar motifs in how the stacks of organic molecules are arranged throughout both structures. These extensive similarities suggest a rather dominating stacking force among the triphenylene units in forming both structures, and they may also explain the relatively smooth transformation of **1** into  $1 \cdot \text{BiCl}_3$ .

In summary, compound  $1 \cdot \text{BiCl}_3$  features a one-dimensional hybrid bismuth(III) chloride network where the Bi–S chelating interaction results in substantial electronic communication between the organic ligand and the metal center. It is an air stable hybrid semiconductor and can be readily synthesized in high yield. The ease of crystallization appears to stem from the relatively weak Bi(III)–Cl bonds linking the organic ligands, and the similar crystalline packing motifs of the reactant (**1**) and the product ( $1 \cdot \text{BiCl}_3$ ). Following this lead, we are now making progress in studying systems with more sophisticated side chains (as compared with the methyl groups in **1**), so as to further address issues such as higher framework dimensionality, electronic band gap tuning, and solution processing.

**Acknowledgment.** We acknowledge the donors of the American Chemical Society Petroleum Research Fund for partial support of this research.

**Supporting Information Available:** Synthesis and crystallization of **1**, full crystallographic data in CIF format for  $1 \cdot \text{BiCl}_3$  and **1**, figures of the crystal structure of **1**, and X-ray powder diffraction patterns for  $1 \cdot \text{BiCl}_3$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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CG049817K